

10049827, 021902

JC07 Rec'd PCT/PTO 19 FEB 2002

FORM PTO-1390  
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

0216-0466P

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/049827

INTERNATIONAL APPLICATION NO. INTERNATIONAL FILING DATE

PCT/JP00/05570

August 18, 2000

PRIORITY DATE CLAIMED

August 19, 1999

TITLE OF INVENTION

POLYETHER POLYURETHANE

APPLICANT(S) FOR DO/EO/US

SHIMIZU, Atsushi; FURUKAWA, Mutsuhisa; KATO, Kiyoo; ASAHINA, Yoshiyuki

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau. WO 01/14444
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is transmitted herewith.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
  - 1.) Declaration of Translation
  - 2.) Twelve (12) sheets of Formal Drawings

U.S. APPLICATION NO (if known, see 37 CFR 1.5) <div style="font-size: 2em; font-weight: bold;">10/049827</div>		INTERNATIONAL APPLICATION NO PCT/JP00/05570		ATTORNEY'S DOCKET NUMBER 0216-0466P	
---	--	--	--	--	--

21. ☒ The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**  
 Neither international preliminary examination fee (37 CFR 1.482)  
 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
 and International Search Report not prepared by the EPO or JPO. .... **\$1,040.00**

International preliminary examination fee (37 CFR 1.482) not paid to  
 USPTO but International Search Report prepared by the EPO or JPO ..... **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
 but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. .... **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
 but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
 and all claims satisfied provisions of PCT Article 33(1)-(4). .... **\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	8 - 20 =	0	X \$18.00	\$	0
Independent Claims	2 - 3 =	0	X \$84.00	\$	0
MULTIPLE DEPENDENT CLAIM(S) (if applicable) None				+ \$280.00	\$ 0
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	890.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are  
 reduced by 1/2.

**SUBTOTAL =**

	\$	890.00
--	----	--------

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(f)).

	\$	0
--	----	---

**TOTAL NATIONAL FEE =**

	\$	890.00
--	----	--------

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

	\$	40.00
--	----	-------

**TOTAL FEES ENCLOSED =**

	\$	930.00
--	----	--------

	<b>Amount to be:</b>	
	<b>refunded</b>	\$
	<b>charged</b>	\$

a. ☒ A check in the amount of \$ 930.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account. No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
 overpayment to Deposit Account No. 02-2448.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:  
**Birch, Stewart, Kolasch & Birch, LLP or Customer No. 2292**  
**P.O. Box 747**  
**Falls Church, VA 22040-0747**  
**(703) 205-8000**

**Date: February 19, 2002**

By

John W. Bailey, #32,881

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: SHIMIZU, Atsushi et al.  
Int'l. Appl. No.: PCT/JP00/05570  
Appl. No.: New Group:  
Filed: February 19, 2002 Examiner:  
For: POLYETHER POLYURETHANE

PRELIMINARY AMENDMENT

**BOX PATENT APPLICATION**

Assistant Commissioner for Patents  
Washington, DC 20231

February 19, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

**AMENDMENTS**

**IN THE SPECIFICATION:**

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/05570 which has an International filing date of August 18, 2000, which designated the United States of America.--

Please replace the paragraph beginning on page 24, line 7, with the following rewritten paragraph:

--Columns: Shodex OH pak SB806M (two columns) and Shodex  
OH pak SB802.5 (one column) (each

Docket No. 0216-0466P

manufactured and sold by Showa Denko K.K.,  
Japan) :--

Please replace the paragraph beginning on page 33, line 18 to page 35, line 2 with the following rewritten paragraph:

--A preferred PTMG used in the present invention as the component (B) has a number average molecular weight of from 500 to 3,000, a molecular weight distribution ( $M_w/M_n$ ) of 1.75 or less, a content of high molecule weight PTMG molecules of from 2 to 5% by weight, and a heteropolyacid content of from 10 to 900 ppb by weight. Following is a method for producing such a preferred PTMG from THF using a heteropolyacid catalyst. In a reaction system where water is present in an amount sufficient to form a THF organic phase and an aqueous THF/catalyst phase having a specific gravity of from 1.8 to 2.3, the retention time ( $V/F$ ) of THF is maintained within the range of from 0.5 to 20 hours, preferably from 0.7 to 15 hours. When the  $V/F$  value is smaller than the above-mentioned range, the conversion of THF is likely to become low. On the other hand, when the  $V/F$  value is larger than the above-mentioned range, the reaction time is likely to become long. With respect to the motive power ( $P/V$ ) applied to the liquid in the reactor, the  $P/V$  value is maintained at  $1.3 \text{ kW/m}^3$  or more, preferably  $1.6 \text{ kW/m}^3$  or more. When the  $P/V$  is smaller than  $1.3 \text{ kW/m}^3$ , the agitation of the reaction system becomes unsatisfactory and the distribution of the diameters of the globules in the reaction system become broad. As a result, the molecular weight

Docket No. 0216-0466P

distribution of the produced PTMG becomes broad and the control of the molecule weight distribution of the PTMG becomes difficult. By appropriately controlling the V/F and P/V values in the above-mentioned method, it is also possible to obtain a PTMG having a number average molecular weight of more than 3,000 and less than or equal to 4,000, and a content of high molecular weight PTMG molecules of more than 5 % by weight and less than or equal to 10 % by weight.--

Please replace the paragraph beginning on page 65 line 17 to page 66, line 15 with the following rewritten paragraph:

--First, a heteropolyacid catalyst solution for use as a polymerization catalyst was produced as follows. A 2-liter reaction vessel was prepared, which is provided with a 3-way cock having three respective ends, wherein each end has attached thereto a condenser and an eggplant type flask for collecting and storing a distillate produced by the condenser, so that the contents of the reaction vessel can be distilled. The thus prepared reaction vessel was used for producing a heteropolyacid catalyst solution. 1 liter of tetrahydrofuran (THF) and 600 g of silicotungstic acid dodecahydrate were introduced into the reaction vessel in this order, and stirred at 60°C, while continuously removing an azeotropic vapor of water and THF from the reaction vessel. The specific gravity of a solution being formed in the reaction vessel was periodically measured while feeding THF to the reaction vessel every 10 minutes so as to

Docket No. 0216-0466P

compensate for the total amount of water and THF removed from the reaction vessel. When the specific gravity of the solution became 2.07, the reaction was terminated to thereby obtain a catalyst solution having a specific gravity of 2.07, namely a solution of heteropolyacid catalyst in a THF/water mixture.--

Please replace the paragraph being on page 70, line 2 with the following rewritten paragraph:

--The obtained PTMG (A) had a number average molecular weight (Mn) of 1840, a molecular weight distribution (Mw/Mn) of 1.60, and a content of high molecular weight PTMG molecules which are at least six times as large as the number average molecular weight of all PTMG molecules (hereinafter, simply referred to as "content of high molecular weight PTMG molecules") of 2.29 % by weight. The number average molecular weight was determined by the terminal titration method, and the molecular weight distribution and the content of high molecular weight PTMG molecules were determined by gel permeation chromatography (GPC) under the conditions mentioned below.--

Please replace the paragraph beginning at page 71, line 21 as with the following rewritten paragraph:

10049827, 021902

Docket No. 0216-0466P

--Columns: Shodex OH pak (manufactured and sold by Showa  
Denko K.K., Japan):  
SB 806 M (2 columns)  
SB 802.5 (1 column) --

Docket No. 0216-0466P

**REMARKS**

The specification has been amended to provide a cross-reference to the previously filed International Application. The specification has also been amended to more clearly explain the purpose of the application and correct typographical errors.

The amendments do not incorporate new matter into the application as originally filed. For example, the amendments at page 24, 34, 66 and 71 simply correct typographical errors. The amendment at page 34 finds support at pages 31-34 of the specification, the amendment at page 66 finds support at page 64, line 11, and the amendment to page 70 finds support at page 34, lines 11-13 of the specification. Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

Attached hereto is a marked-up version of the changes made to the application by this Amendment.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By 

John W. Bailey, #32,881

JWB/cqc  
0216-0466P

P.O. Box 747  
Falls Church, VA 22040-0747  
(703) 205-8000



Docket No. 0216-0466P

VERSION WITH MARKINGS TO SHOW CHANGES MADE

The paragraph beginning at page 24, line 7 has been amended as follow:

Columns: Shodex OH [pack]pak SB806M (two columns) and  
Shodex OH [pack]pak SB802.5 (one column)  
(each manufactured and sold by Showa Denko  
K.K., Japan):

The paragraph beginning on page 33, line 18 to page 35, line 2 has been amended as follows:

A preferred PTMG used in the present invention as the component (B) has a number average molecular weight of from 500 to 3,000, a molecular weight distribution (Mw/Mn) of 1.75 or less, a content of high molecule weight PTMG molecules of from 2 to 5% by weight, and a heteropolyacid content of from 10 to 900 ppb by weight. Following is a method for producing such a preferred PTMG from THF using a heteropolyacid catalyst. In a reaction system where water is present in an amount sufficient to form a THF organic phase and an aqueous THF/catalyst phase having a specific gravity of from 1.8 to 2.3, the retention time (V/F) of THF is maintained within the range of from 0.5 to 20 hours, preferably from 0.7 to 15 hours. When the V/F value is smaller than the above-mentioned range, the conversion of THF is likely to become

Docket No. 0216-0466P

low. On the other hand, when the V/F value is larger than the above-mentioned range, the reaction time is likely to become long. With respect to the motive power (P/V) applied to the liquid in the reactor, the P/V value is maintained at 1.3 kW/m<sup>3</sup> or more, preferably 1.6 kW/m<sup>3</sup> or more. When the P/V is smaller than 1.3 kW/m<sup>3</sup>, the agitation of the reaction system becomes unsatisfactory and the distribution of the diameters of the globules in the reaction system become broad. As a result, the molecular weight distribution of the produced PTMG becomes broad and the control of the molecule weight distribution of the PTMG becomes difficult. By appropriately controlling the V/F and P/V values in the above-mentioned method, it is also possible to obtain a PTMG having a number average molecular weight of more than 3,000 and less than or equal to 4,000, and a content of high molecular weight PTMG molecules of more than 5 % by weight and less than or equal to 10 % by weight.

The paragraph beginning on page 65, line 17 to page 66, line 15 has been amended as follows:

First, a heteropolyacid catalyst solution for use as a polymerization catalyst was produced as follows. A 2-liter reaction vessel was prepared, which is provided with a 3-way cock having three respective ends, wherein each end has attached thereto a condenser and an eggplant type flask for collecting and storing a distillate produced by the condenser, so that the contents of the reaction vessel can be distilled. The thus prepared reaction vessel was used for producing a heteropolyacid

Docket No. 0216-0466P

catalyst solution. 1 liter of tetrahydrofuran (THF) and 600 g of silicotungstic acid dodecahydrate were introduced into the reaction vessel in this order, and stirred at 60°C, while continuously removing an azeotropic vapor of water and THF from the reaction vessel. The specific gravity of a solution being formed in the reaction vessel was periodically measured while feeding THF to the reaction vessel every 10 minutes so as to compensate for the total amount of water and THF removed from the reaction vessel. When the specific gravity of the solution became 2.07, the reaction was terminated to thereby obtain a catalyst solution having a specific gravity of [2.01]2.07, namely a solution of heteropolyacid catalyst in a THF/water mixture.

The paragraph being on page 70, line 2 has been amended as follows:

The obtained PTMG (A) had a number average molecular weight (Mn) of 1840, a molecular weight distribution (Mw/Mn) of 1.60, and a content of high molecular weight PTMG molecules which are at least six times as large as the number average molecular weight of all PTMG molecules (hereinafter, simply referred to as "content of high molecular weight PTMG molecules") of 2.29 % by weight. [These values were determined by gel permeation chromatography (GPC) under the conditions mentioned below] The number average molecular weight was determined by the terminal titration method, and the molecular weight distribution and the content of high

Docket No. 0216-0466P

molecular weight PTMG molecules were determined by gel permeation chromatography (GPC) under the conditions mentioned below.

The paragraph beginning at page 71, line 21 has been amended as follows:

Columns: Shodex OH [pack]pak (manufactured and sold by Showa Denko K.K., Japan):  
SB 806 M (2 columns)  
SB 802.5 (1 column) --

(Rev. 11/13/01)

12/1/02

1

TITLE OF THE INVENTION

Polyether polyurethane

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to a polyether polyurethane. More particularly, the present invention is concerned with a polyether polyurethane comprising (A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate; (B) a specific polyoxytetramethylene glycol (PTMG); and (C) at least one chain extender selected from the group consisting of a C<sub>2</sub>-C<sub>10</sub> polyol having two or more hydroxyl groups and a C<sub>2</sub>-C<sub>10</sub> polyamine having two or more amino groups. The polyether polyurethane of the present invention exhibits excellent properties including high elastic modulus, excellent elastic properties at low temperatures and high flexibility, as compared to the conventional polyether polyurethanes. By virtue of these excellent properties, the polyether polyurethane of the present invention can be advantageously used in various application fields where conventional polyether polyurethanes are used.

25 Further, the present invention is also concerned with a

urethane prepolymer comprising (A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate; and (B) a specific polyoxytetramethylene glycol (PTMG), wherein the urethane prepolymer has terminal isocyanate groups.

#### Prior Art

In the production of polyether polyurethanes, various types of diols are used to control the properties thereof. For example, a low molecular weight diol is used in combination with a high molecular weight diol, such as a polyether diol, a polyester diol or a polycarbonate diol. Specific examples of polyether diols include polyoxyethylene glycol, polyoxypropylene glycol, polyoxytetramethylene glycol and modified high molecular weight diols obtained therefrom. Of the above-exemplified polyether diols, polyoxytetramethylene glycol has been used as a component constituting a soft segment of a shaped polyether polyurethane article or a polyether polyurethane elastic fiber since a long time ago.

A polyether polyurethane is produced from a polyisocyanate, a high molecular weight diol and a low molecular weight diol as main raw materials, and is a

block copolymer having a soft segment composed mainly of the high molecular weight diol and a hard segment composed mainly of the polyisocyanate and the low molecular weight diol. By virtue of such structure, the polyether polyurethane exhibits rubber elasticity. The chemical composition, length of the polymer blocks, and secondary and tertiary structures of the polyether polyurethane depend mainly on the types of the polyisocyanate and the high molecular weight diol used, and have a large influence on the physical properties of an ultimate polyether polyurethane product. Especially, the choice of the soft segment is a very important factor in fields where a product obtained from a polyether polyurethane, such as an elastic fiber or a polyurethane elastomer, is required to have excellent and precisely controlled mechanical properties and viscoelastic properties.

As a conventional technique for obtaining a polyoxytetramethylene glycol (PTMG) which has been used as a high molecular weight diol, a method disclosed in Unexamined Japanese Patent Application Laid-Open Specification No. 59-215320 (corresponding to U.S. Patent No. 4,568,775 and EP 126471) is known. Further, Unexamined Japanese Patent Application Laid-Open Specification No. 61-123626 (corresponding to U.S. Patent No. 4,658,065

and EP 158229) and Unexamined Japanese Patent Application Laid-Open Specification No. 59-221326 (corresponding to U.S. Patent No. 4,568,775 and EP 126471) have a description concerning the molecular weight distributions of the produced PTMG's. With respect to the techniques for removing the oligomers contained in a PTMG, Unexamined Japanese Patent Application Laid-Open Specification No. 61-123629 (corresponding to U.S. Patent No. 4,677,231 and EP 181621) discloses a method in which a thin film evaporator is used, and Unexamined Japanese Patent Application Laid-Open Specification No. 60-108424 discloses a method in which oligomers are separated from the PTMG by using water and an alcoholic solvent. In addition, with respect to the techniques for adjusting the content of a polymerization catalyst remaining in a PTMG, Unexamined Japanese Patent Application Laid-Open Specification No. 61-118420 (corresponding to U.S. Patent No. 4,677,231 and EP 181621) and Unexamined Japanese Patent Application Laid-Open Specification No. 61-115934 (corresponding to U.S. Patent No. 4,677,231 and EP 181621) disclose a method in which a hydrocarbon or a halogenated hydrocarbon as an organic solvent is added to a PTMG to thereby separate the residual catalyst therefrom; and Unexamined Japanese Patent Application Laid-Open Specification No.



61-123629 (corresponding to U.S. Patent No. 4,677,231 and EP 181621) discloses a method in which an adsorbent is used to remove the catalyst.

5 The characteristics (such as molecular weight, molecular weight distribution, oligomer content and residual catalyst content) of the PTMG used as a raw material for a polyether polyurethane are considered as important factors which affect the quality of the final polyether polyurethane. However, heretofore, no details are known in the art about how the characteristics of the PTMG influence the physical properties of the final polyether polyurethane. In addition, no polyether polyurethanes are known, which have been adjusted, by strictly controlling the characteristics of the raw material PTMG, so as to have a good balance of various excellent properties.

10

15

Nowadays, polyether polyurethane is an important material which is used in a wide variety of fields, and the application field thereof is expected to become more extensive. Accordingly, there has always been a demand for improvement in the quality of the polyether polyurethane. Further, improvements in different properties of the polyether polyurethane are, respectively, desired in different application fields. For example, a polyether polyurethane used as a thermoplastic elas-

20

25

5 tomer is required to exhibit high elastic modulus, excellent characteristics at low temperatures, small compression set, excellent surface touch with respect to an ultimate shaped product produced therefrom, and convenience in practical use of a coating composition containing the polyether polyurethane. Similarly, in the industrial fields related to a flexible foam and a rigid foam, an RIM (Reaction Injection Molding) product, an R-RIM (Reinforced Reaction Injection Molding) product, a coating composition, an adhesive, a binder, a sealant, a fiber stock, an artificial leather and a wide variety of other polyurethane products, and in various other industrial fields related to polyurethane urea products, there has been a demand for the improvements in the properties of a polyether polyurethane.

#### SUMMARY OF THE INVENTION

20 In this situation, the present inventors have made extensive and intensive studies with a view toward solving the above-mentioned problems. As a result, it has unexpectedly been found that a polyether polyurethane, which comprises (A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate, (B) a poly-

oxytetramethylene glycol (PTMG) having a specific molecular weight, a specific molecular weight distribution and a specific content of high molecular weight molecules, which PTMG, notwithstanding low viscosity thereof, exhibits high heat resistance, and (C) at least one chain extender selected from the group consisting of a  $C_2$ - $C_{10}$  polyol having two or more hydroxyl groups and a  $C_2$ - $C_{10}$  polyamine having two or more amino groups, exhibits high elastic modulus, excellent elastic properties at low temperatures and high flexibility, as compared to the conventional polyether polyurethanes.

The present invention has been completed, based on this novel finding.

Accordingly, it is an object of the present invention to provide a polyether polyurethane having high elastic modulus, excellent elastic properties at low temperatures and high flexibility.

It is another object of the present invention to provide a urethane prepolymer which can be used as a raw material for obtaining a polyether polyurethane having high elastic modulus, excellent elastic properties at low temperatures and high flexibility.

The foregoing and other objects, features and advantages of the present invention will be apparent to those skilled in the art from the following detailed

description and appended claims taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

5           In the drawings:

Fig. 1 is a schematic diagram showing the production system used in Reference Examples 1 and 2 for producing the specific polyoxytetramethylene glycol (PTMG) used in the present invention;

10           Fig. 2 is a chromatogram of PTMG (A) produced in Reference Example 1, which shows the molecular weight distribution of PTMG (A), wherein the abscissa shows the logarithm (log) of the molecular weight, the ordinate shows the weight % of component PTMG molecules, based on the total weight of all PTMG molecules, the  
15           intersection of the vertical straight broken line and the abscissa shows the logarithm of the number average molecular weight, and the area of the hatched portion shows the amount of the PTMG molecules having molecular  
20           weights which are at least six times as large as the number average molecular weight of all PTMG molecules;

Fig. 3 is a graph showing the stress-strain curves of polyether polyurethanes, wherein each O represents the polyether polyurethane produced in Example 6, each  
25           Δ represents the polyether polyurethane produced in

Comparative Example 8, each  $\square$  represents the polyether polyurethane produced in Comparative Example 9, each  $\bullet$  represents the polyether polyurethane produced in Comparative Example 10, and each  $\blacktriangle$  represents the polyether polyurethane produced in Comparative Example 11;

Fig. 4 is a graph showing the temperature dependencies of the dissipation factors ( $\tan \delta$ ) of polyether polyurethanes, wherein each  $\circ$  represents the polyether polyurethane produced in Example 6, each  $\Delta$  represents the polyether polyurethane produced in Comparative Example 8, each  $\square$  represents the polyether polyurethane produced in Comparative Example 9, each  $\bullet$  represents the polyether polyurethane produced in Comparative Example 10, and each  $\blacktriangle$  represents the polyether polyurethane produced in Comparative Example 11;

Fig. 5 is a graph showing the temperature dependencies of the storage elastic moduli ( $E'$ ) of polyether polyurethanes, wherein each  $\circ$  represents the polyether polyurethane produced in Example 6, each  $\Delta$  represents the polyether polyurethane produced in Comparative Example 8, each  $\square$  represents the polyether polyurethane produced in Comparative Example 9, each  $\bullet$  represents the polyether polyurethane produced in Comparative Example 10, and each  $\blacktriangle$  represents the polyether polyurethane produced in Comparative Example 11;

Figs. 6(a) to 6(j) are polarization photomicrographs of polyether polyurethanes, wherein Figs. 6(a) and 6(b) are polarization photomicrographs of the polyether polyurethane produced in Example 6, Figs. 6(c) and 6(d) are polarization photomicrographs of the polyether polyurethane produced in Comparative Example 8, Figs. 6(e) and 6(f) are polarization photomicrographs of the polyether polyurethane produced in Comparative Example 9, Figs. 6(g) and 6(h) are polarization photomicrographs of the polyether polyurethane produced in Comparative Example 10, and Figs. 6(i) and 6(j) are polarization photomicrographs of the polyether polyurethane produced in Comparative Example 11, and wherein the polarization photomicrographs of Figs. 6(b), 6(d), 6(f), 6(h) and 6(j) are taken using a sensitive color plate; and

Figs. 7(a) to 7(d) are polarization photomicrographs of polyether polyurethanes, wherein Figs. 7(a) and 7(b) are polarization photomicrographs of the polyether polyurethane produced in Example 7, and Figs. 7(c) and 7(d) are polarization photomicrographs of the polyether polyurethane produced in Comparative Example 12, and wherein the polarization photomicrographs of Figs. 7(b) and 7(d) are taken using a sensitive color plate.

Description of Reference Numerals

- 1: stirrer  
2: reactor  
5 3: water feeding tank  
4: first, phase-separation vessel  
5: distillation vessel  
6: second, phase-separation vessel  
7: adsorption column  
10 8: distillation column  
9: third, phase-separation vessel  
10: vacuum distillation vessel

DETAILED DESCRIPTION OF THE INVENTION

15 In one aspect of the present invention, there is provided a polyether polyurethane comprising:

(A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an  
20 aliphatic polyisocyanate;

(B) a polyoxytetramethylene glycol (PTMG); and

(C) at least one chain extender selected from the group consisting of a C<sub>2</sub>-C<sub>10</sub> polyol having two or more hydroxyl groups and a C<sub>2</sub>-C<sub>10</sub> polyamine having two or  
25 more amino groups,

wherein the PTMG has the following characteristics

(1) to (3):

(1) a number average molecular weight of from 500 to 4,000;

5 (2) a molecular weight distribution of 1.75 or less in terms of the Mw/Mn ratio, wherein Mw represents the weight average molecular weight of PTMG and Mn represents the number average molecular weight of PTMG; and

10 (3) a content of high molecular weight PTMG molecules of 10 % by weight or less, based on the total weight of all PTMG molecules, wherein the high molecular weight PTMG molecules are defined as PTMG molecules having molecular weights which are at least six times  
15 as large as the number average molecular weight of all PTMG molecules.

In another aspect of the present invention, there is provided a urethane prepolymer comprising:

20 (A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate; and

(B) a polyoxytetramethylene glycol (PTMG),

the urethane prepolymer having terminal isocyanate  
25 groups,



wherein the PTMG has the following characteristics  
(1) to (3):

(1) a number average molecular weight of from 500  
to 4,000;

5       (2) a molecular weight distribution of 1.75 or  
less in terms of the Mw/Mn ratio, wherein Mw represents  
the weight average molecular weight of PTMG and Mn rep-  
resents the number average molecular weight of PTMG;  
and

10       (3) a content of high molecular weight PTMG mo-  
lecules of 10 % by weight or less, based on the total  
weight of all PTMG molecules, wherein the high molecu-  
lar weight PTMG molecules are defined as PTMG molecules  
having molecular weights which are at least six times  
15       as large as the number average molecular weight of all  
PTMG molecules.

For easy understanding of the present invention,  
the essential features and various embodiments of the  
20       present invention are enumerated below.

1. A polyether polyurethane comprising:

(A) at least one polyisocyanate having two or  
more isocyanate groups, which is selected from the  
25       group consisting of an aromatic polyisocyanate and an

aliphatic polyisocyanate;

(B) a polyoxytetramethylene glycol (PTMG); and

(C) at least one chain extender selected from the group consisting of a C<sub>2</sub>-C<sub>10</sub> polyol having two or more hydroxyl groups and a C<sub>2</sub>-C<sub>10</sub> polyamine having two or more amino groups,

wherein the PTMG has the following characteristics

(1) to (3):

(1) a number average molecular weight of from 500 to 4,000;

(2) a molecular weight distribution of 1.75 or less in terms of the Mw/Mn ratio, wherein Mw represents the weight average molecular weight of PTMG and Mn represents the number average molecular weight of PTMG;

and

(3) a content of high molecular weight PTMG molecules of 10 % by weight or less, based on the total weight of all PTMG molecules, wherein the high molecular weight PTMG molecules are defined as PTMG molecules having molecular weights which are at least six times as large as the number average molecular weight of all PTMG molecules.

2. The polyether polyurethane according to item 1

above, wherein the PTMG has a heteropolyacid content of

from 10 to 900 ppb by weight.

3. The polyether polyurethane according to item 1 above, wherein the content of high molecular weight PTMG molecules in the PTMG is 2 to 5 % by weight.

4. A urethane prepolymer comprising:

(A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate; and

(B) a polyoxytetramethylene glycol (PTMG), the urethane prepolymer having terminal isocyanate groups,

wherein the PTMG has the following characteristics (1) to (3):

(1) a number average molecular weight of from 500 to 4,000;

(2) a molecular weight distribution of 1.75 or less in terms of the Mw/Mn ratio, wherein Mw represents the weight average molecular weight of PTMG and Mn represents the number average molecular weight of PTMG; and

(3) a content of high molecular weight PTMG molecules of 10 % by weight or less, based on the total

weight of all PTMG molecules, wherein the high molecular weight PTMG molecules are defined as PTMG molecules having molecular weights which are at least six times as large as the number average molecular weight of all PTMG molecules.

5        5.    The urethane prepolymer according to item 4 above, wherein the PTMG has a heteropolyacid content of from 10 to 900 ppb by weight.

10       6.    The urethane prepolymer according to item 4 above, wherein the content of high molecular weight PTMG molecules in the PTMG is 2 to 5 % by weight.

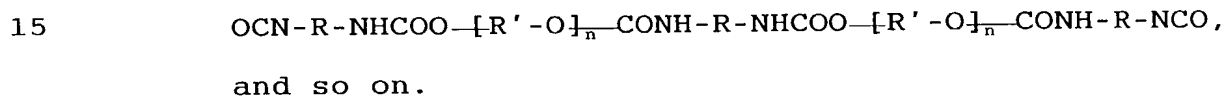
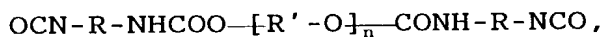
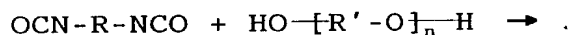
15       7.    The urethane prepolymer according to item 4 above, wherein the terminal isocyanate groups are partly or wholly modified to have at least one functional group other than an isocyanate group, wherein the at least one functional group is introduced to the terminal isocyanate groups by addition.

20

8.    The urethane prepolymer according to item 7 above, wherein the functional group is selected from the group consisting of a (meth)acryloyl group and a silyl group.

Hereinbelow, the polyether polyurethane of the present invention will be described in detail.

The polyether polyurethane of the present invention comprises (A) a polyisocyanate, (B) a polyoxy-tetramethylene glycol (PTMG), and (C) a polyol and/or a polyamine. A "polyether polyurethane" is a polyurethane containing a polyether diol as its polymeric polyol component (a soft segment). For example, when a diisocyanate and a polyether diol are reacted with each other, urethane linkage-containing prepolymers having different molecular weights are obtained as shown below.



When such a prepolymer is reacted with a C<sub>2</sub>-C<sub>10</sub> polyol and/or a C<sub>2</sub>-C<sub>10</sub> polyamine as a chain extender, a polyether polyurethane is obtained. For example, when a low molecular weight diol is used as a chain extender, a urethane linkage (-NH-CO-O-) is formed in the resultant polyether polyurethane. On the other hand, when a low molecular weight diamine is used as a chain extender, a urea linkage (-NH-CO-NH-) is formed in the

resultant polyether polyurethane.

The polyisocyanate used as component (A) of the polyether polyurethane of the present invention is at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate. There is no limitation with respect to the number of carbon atoms of the polyisocyanate. For example, an aromatic diisocyanate, an aliphatic diisocyanate, and a polyisocyanate modified with a polyol or the like can be used.

Examples of aromatic diisocyanates include 4,4'-diphenylmethane diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1,5-naphthalene diisocyanate and xylylene diisocyanate.

Examples of aliphatic diisocyanates include diisocyanates obtained by hydrogenating the aromatic rings of the aromatic diisocyanates exemplified above, hexamethylene diisocyanate, isophorone diisocyanate and 4,4-cyclohexyl diisocyanate.

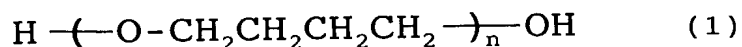
Examples of modified polyisocyanates include isocyanurate type polyisocyanates.

Further examples of polyisocyanates usable as component (A) include blocked isocyanates obtained by

modifying the isocyanate groups of any of the above-mentioned polyisocyanates with an oxime compound and the like.

5 In the present invention, the above-mentioned polyisocyanates, i.e., the aromatic diisocyanates, the aliphatic diisocyanates and the modified diisocyanates, and the like, can be used individually or in combination as the polyisocyanate (A).

10 The component (B) of the polyether polyurethane of the present invention is a polyoxytetramethylene glycol (PTMG). The PTMG used in the present invention is a diol obtained by subjecting tetrahydrofuran to ring-opening polymerization in the presence of a heteropolyacid catalyst. Illustratively stated, the PTMG is  
15 a mixture of polymer chains each independently represented by the following formula (1):



wherein, n is independently an integer of from 2 to 4,000, preferably from 2 to 2,100.

20 It should be noted that there is no need for the PTMG molecules to have all molecular weights in the range of from 2 to 4,000 in terms of the value of n.

The PTMG used in the present invention is a PTMG having the following characteristics (1) to (3):

(1) a number average molecular weight of from 500 to 4,000;

(2) a molecular weight distribution of 1.75 or less in terms of the  $M_w/M_n$  ratio, wherein  $M_w$  represents the weight average molecular weight of PTMG and  $M_n$  represents the number average molecular weight of PTMG; and

(3) a content of high molecular weight PTMG molecules of 10 % by weight or less, based on the total weight of all PTMG molecules, wherein the high molecular weight PTMG molecules are defined as PTMG molecules having molecular weights which are at least six times as large as the number average molecular weight of all PTMG molecules.

In the present invention, it is important that the PTMG has the above-mentioned specific number average molecular weight, specific molecular weight distribution and specific content of high molecular weight PTMG molecules, and exhibits not only high heat resistance, but also low viscosity. When a polyether polyurethane is produced using such a PTMG, the polyether polyurethane exhibits a good balance of greatly improved properties as compared to that of a polyether polyurethane produced using a conventional PTMG. Illustratively stated, such a polyether polyurethane exhibits



high elasticity and elastic recovery, low permanent compression set, and excellent low-temperature characteristics, as compared to those of the conventional polyether polyurethane. Further, when a shaped article is produced from the polyether polyurethane of the present invention, there is no tack on the surface of the produced shaped articles.

From the viewpoint of the balance of flexibility and elastic modulus of the polyether polyurethane produced using the PTMG, the number average molecular weight of the PTMG used in the present invention is in the range of from 500 to 4,000, preferably from 750 to 3,500, more preferably from 800 to 3,500, most preferably from 800 to 3,000. The number average molecular weight of the PTMG can be determined, for example, by gel permeation chromatography (GPC) or by a terminal titration method. In preferred examples of the present invention, however, the number average molecular weight is calculated from the OH value determined by the terminal titration method.

When the number average molecular weight of the PTMG is less than 500, the flexibility of the polyether polyurethane becomes unsatisfactory, and when the number average molecular weight of the PTMG is higher than 4,000, the elastic modulus of the polyether poly-

urethane becomes unsatisfactory.

The molecular weight distribution of the PTMG used in the present invention is 1.75 or less, preferably 1.15 to 1.75, more preferably 1.15 to 1.70. In the present invention, the molecular weight distribution is defined as the  $M_w/M_n$  ratio, wherein  $M_w$  represents the weight average molecular weight of the PTMG and  $M_n$  represents the number average molecular weight of the PTMG. The  $M_w$  and the  $M_n$  values can be determined by GPC using the apparatuses and the conditions which are described below in the Examples. When the molecular weight distribution ( $M_w/M_n$  ratio) of a PTMG is 1.75 or less, the viscosity of the PTMG is satisfactorily low, and a polyether polyurethane produced using such a PTMG exhibits a good balance of excellent elongation at break and excellent tensile strength at break. On the other hand, when a polyether polyurethane is produced using a PTMG having a molecular weight distribution ( $M_w/M_n$  ratio) of more than 1.75, the mechanical properties (such as strength and elongation) of the polyether polyurethane become low. In addition, since the soft segment composed of a PTMG having such a broad molecular weight distribution inevitably contains a large amount of high molecular weight PTMG molecules, the high molecular weight PTMG molecules hinder the phase separation of

the soft segment and the hard segment in the polyether polyurethane, thereby causing the low-temperature characteristics of the polyether polyurethane to become poor. Theoretically, the lower limit of the molecular weight distribution is 1.0; however, in practice, it is difficult to produce a PTMG having a molecular weight distribution of less than 1.15.

The PTMG used in the present invention has a content of high molecular weight PTMG molecules of 10 % by weight or less, based on the total weight of all PTMG molecules. In the present invention, the "high molecular weight PTMG molecules" are defined as PTMG molecules having molecular weights which are at least six times as large as the number average molecular weight of all PTMG molecules. The PTMG is a mixture of molecules (i.e., polymer chains) having different molecular weights. A PTMG molecule having a molecular weight which is more than six times the number average molecular weight of all PTMG molecules has a melting point which is at least twice as high as that of the mixture of all PTMG molecules. Accordingly, when a large amount of high molecular weight PTMG molecules is contained in the PTMG, the high molecular weight PTMG molecules hinder the phase separation of the soft segment and the hard segment in the polyether polyurethane. In

the present invention, the content of high molecular weight PTMG molecules and the molecular weight distribution can be determined by GPC under the following conditions:

- 5           Apparatus: Shodex GPC system-11 (manufactured and sold by Showa Denko K. K., Japan);
- Columns: Shodex OH pack SB806M (two columns) and Shodex OH pack SB802.5 (one column) (each manufactured and sold by Showa Denko K. K.,
- 10                   Japan);
- Detector: Differential refractometer;
- Temperature: 60 °C;
- Carrier: 0.02 mol/liter solution of LiBr in dimethylacetamide;
- 15           Flow rate of the carrier: 1.0 ml/min;
- Sample: 100 µl of 0.8% PTMG solution in the carrier; and
- Molecular weight standards: PTMG, Mn = 547,000 (Mw/Mn = 1.35), Mn = 283,000 (Mw/Mn = 1.08), Mn = 99,000 (Mw/Mn = 1.08), Mn = 67,000 (Mw/Mn = 1.04),
- 20                   Mn = 35,500 (Mw/Mn = 1.06), Mn = 15,000 (Mw/Mn = 1.09), Mn = 6,700 (Mw/Mn = 1.13), Mn = 2,170 (Mw/Mn = 1.12), Mn = 1,300 (Mw/Mn = 1.12), Mn = 650 (Mw/Mn = 1.18), and THF monomer.
- 25           In the PTMG used in the present invention, the

content of high molecular weight PTMG molecules is 10 %  
by weight of less and, thus, the PTMG is in the form of  
a uniform PTMG mixture having a low viscosity. When  
such a PTMG is used in the polymerization reaction for  
5 producing a polyether polyurethane, a high polymeriza-  
tion rate can be achieved. In addition, the use of  
such a PTMG is also advantageous in that the obtained  
polyether polyurethane exhibits high elastic modulus.  
It is considered that the decrease in the amount of  
10 high molecular weight PTMG molecules leads to an im-  
provement in fluidity of the polyether polyurethane and  
facilitates the formation of a structure in which the  
phase separation between the hard segment and the soft  
segment occurs. Further, the ease in formation of such  
15 a structure is considered to be increased correlatively  
with an increase in the ease in formation of spheru-  
lites which are considered to be formed by the hard  
segment.

The high molecular weight PTMG molecules are con-  
20 sidered to improve the heat stability of the PTMG as a  
whole through interaction with low molecular weight  
PTMG molecules which have high heat decomposability.  
Therefore, in the present invention, it is preferred  
that a small amount of high molecular weight PTMG mo-  
25 lecules is present in the PTMG used. Specifically, the

content of the high molecular weight PTMG molecules is preferably in the range of from 2 to 5 % by weight, more preferably 2 to 3.5 % by weight, most preferably 2 to 3 % by weight. When the content of the high molecular weight PTMG molecules is less than 2 % by weight, the above-mentioned effect of the high molecular weight PTMG molecules to improve heat resistance becomes unsatisfactory.

It is preferred that the PTMG used in the present invention has a heteropolyacid content of from 10 to 900 ppb by weight (1 ppb by weight is  $1 \times 10^{-9}$ ). As mentioned above, the PTMG used in the present invention is obtained by the ring-opening polymerization of tetrahydrofuran in the presence of a heteropolyacid catalyst, and the heteropolyacid contained in the PTMG is the residual polymerization catalyst.

A heteropolyacid is an acid obtained by the condensation of an oxide of at least one metal species selected from the group consisting of molybdenum (Mo), tungsten (W) and vanadium (V), and an oxyacid of at least one element other than mentioned above, such as phosphorus (P), silicon (Si), arsenic (As), germanium (Ge), boron (B), titanium (Ti), cerium (Ce), cobalt (Co) and niobium (Nb). The atomic ratio of the metal species (any one or more of metals selected from the

group consisting of Mo, W and V) contained in the heteropolyacid to other elements in the heteropolyacid is 2.5 to 12.

The heteropolyacid contained in the PTMG may be in the form of a salt. Specific examples of heteropolyacids include phosphomolybdic acid, phosphotungstic acid, phosphomolybdotungstic acid, phosphomolybdovanadic acid, phosphomolybdotungstovanadic acid, phosphotungstovanadic acid, phosphomolybdoniobic acid, silicotungstic acid, silicomolybdic acid, silicomolybdotungstic acid, silicomolybdotungstovanadic acid, germanotungstic acid, borotungstic acid, boromolybdic acid, boromolybdotungstic acid, boromolybdovanadic acid, boromolybdotungstovanadic acid, cobaltmolybdic acid, cobalttungstic acid, arsenomolybdic acid, arsenotungstic acid, titanomolybdic acid and ceromolybdic acid, and metal salts thereof.

The heteropolyacid content of the PTMG is defined as the total concentration of molybdenum, tungsten and vanadium (ions) which are present in the PTMG. The concentrations of molybdenum, tungsten and vanadium in the PTMG are determined by ICP-Mass spectrometry.

The heteropolyacid content of the PTMG is preferably in the range from 10 to 900 ppb by weight, and the PTMG having a heteropolyacid content within this range

exhibits excellent heat stability, and is capable of suppressing depolymerization thereof even at high temperatures. When the heteropolyacid content of the PTMG is less than 10 ppb by weight, the heteropolyacid is incapable of improving the heat stability of the PTMG. On the other hand, when the heteropolyacid content of the PTMG is more than 900 ppb by weight, the produced polyether polyurethane is likely to suffer discoloration at high temperatures. Further, since a part of the heteropolyacid is crystallized to thereby promote depolymerization of the PTMG, the weatherability, light resistance, oxidation resistance and the like of ultimate products obtained from such a polyether polyurethane become low.

For producing the polyether polyurethane of the present invention, it is preferred to use a PTMG which has a low content of oligomers, i.e., tetramer and any smaller oligomers than tetramer. With respect to the structure of the oligomers, linear oligomers and cyclic oligomers are generally present in a PTMG. In a polyether polyurethane, a moiety composed of a linear PTMG oligomer has a chain length and a molecular structure which are intermediate between those of a soft segment (composed of long-chain components) and a hard segment (composed of short-chain components). Such a moiety



composed of a linear oligomer may hinder the formation of a structure in which the phase separation between the hard segment and the soft segment occurs. Further, a cyclic oligomer is likely to lower the drying characteristic of a polyether polyurethane coating and such a coating is likely to exhibit tack on the surface thereof.

Hereinbelow, an explanation is made of one example of a method for producing the PTMG used in the present invention.

The PTMG having the above-mentioned specific molecular weight, specific molecular weight distribution and specific content of high molecular weight PTMG molecules can be synthesized in the following manner.

The PTMG can be produced by conducting a continuous polymerization reaction in a two-phase system comprising a reaction-formed raw material tetrahydrofuran organic phase containing a polymer and a reaction-formed aqueous tetrahydrofuran/heteropolyacid catalyst phase, while controlling the retention time and the retention time distribution of the monomer (tetrahydrofuran) in the catalyst phase so as to control the molecular weight distribution of the polymer (PTMG).

As an example of a preferred method for producing the PTMG used in the present invention, there can be

mentioned a method which comprises a polymerization step (to perform a ring-opening polymerization of tetrahydrofuran to produce the PTMG) conducted using a continuous reactor equipped with a stirrer, and a subsequent step for adjusting the residual heteropolyacid content of the produced PTMG. In the polymerization step for performing a ring-opening polymerization of tetrahydrofuran (hereinafter, referred to simply as "THF") in the presence of a heteropolyacid catalyst, the reaction system comprises the following two phases: a raw material THF organic phase and an aqueous THF/heteropolyacid catalyst phase having a specific gravity of from 1.8 to 2.3. The heteropolyacid is sparingly soluble in an anhydrous THF, but well soluble in a mixed solvent prepared by adding a small amount of water to THF. When a heteropolyacid solution having a specific gravity of from 1.8 to 2.3 which has been prepared by dissolving a heteropolyacid in the mixed solvent of water and THF is added to THF, the resultant reaction system separates into two phases, namely a THF organic phase and an aqueous THF/heteropolyacid catalyst phase (hereinafter, frequently referred to as "aqueous THF/catalyst phase" or simply as "catalyst phase") having a specific gravity of from 1.8 to 2.3. The reason why such a reaction system is obtained is

not fully elucidated, but considered to be that a small amount of water is coordinated to the heteropolyacid.

In the polymerization reaction performed in the above-mentioned reaction system comprising a THF organic phase and an aqueous THF/catalyst phase, the molecular weight distribution, especially the content of high molecular weight PTMG molecules, of the produced PTMG can be adjusted by appropriately controlling the rate (F) ( $\text{m}^3/\text{hour}$ ) of feeding THF to the reactor, the motive power (P) (kW) applied to the liquid in the reactor, the volume (V) ( $\text{m}^3$ ) of the liquid in the reactor, and the amount of the heteropolyacid catalyst used. The synthesis of PTMG is conducted by a reaction between a reaction-formed THF organic phase containing a polymer and a reaction-formed aqueous THF/catalyst phase. The reaction system is an emulsion in which the reaction-formed THF organic phase and the reaction-formed aqueous THF/catalyst phase are mutually dispersed in each other both in the form of globules. The polymerization of PTMG is considered to take place in the aqueous THF/catalyst phase. In accordance with the progress of the polymerization reaction, the PTMG dissolved in the aqueous THF/catalyst phase is partitioned between the aqueous THF/catalyst phase and the THF organic phase, and the state of partition reaches an

equilibrium under the reaction conditions and becomes stationary. In such a reaction system, when the retention time  $V/F$  (hr) of THF (raw material) in the reactor is increased, the retention time distribution of THF in the aqueous THF/catalyst phase becomes broad, and the amount of high molecular weight PTMG molecules increases. Contrary to the above, when the  $V/F$  value is decreased, the retention time distribution of THF in the aqueous THF/catalyst phase becomes narrow, and the amount of high molecular weight PTMG molecules decreases. Further, when it is intended to control the molecular weight distribution of the PTMG without varying the number average molecular weight thereof, the amount of heteropolyacid catalyst may be adjusted in accordance with the variation of the  $V/F$  value so as to maintain at a constant value the average retention time of THF as viewed per equivalent of the catalyst.

With respect to the motive power  $P/V$  ( $\text{kW}/\text{m}^3$ ) applied to the liquid in the reactor, when the value of  $P/V$  is varied, the average particle diameters of globules of the aqueous THF/catalyst phase and the THF organic phase become varied. This variation in the average particle diameters of the globules is considered to result in a variation in the area of contact between the aqueous THF/catalyst phase and the THF organic

phase, as well as a variation in the frequency of the coalescence and redivision of the above-mentioned globules, to thereby change the amounts of substances which are moving between the catalyst phase and the organic phase. Specifically, when the P/V value is increased, the amounts of substances which are moving between the catalyst phase and the organic phase become increased, and this increase causes the retention time of the THF monomer molecules in the catalyst phase to become uniform. As a result, it is considered that the retention time distribution of THF in the catalyst phase becomes narrow and the number of high molecular weight PTMG molecules becomes decreased. Contrary to the above, the decrease in the P/V value causes the retention time distribution of THF in the catalyst phase to become broad and causes the number of high molecular weight PTMG molecules to become increased.

A preferred PTMG used in the present invention as the component (B) has a number average molecular weight of from 500 to 3,000, a molecular weight distribution (Mw/Mn) of 1.75 or less, a content of high molecular weight PTMG molecules of from 2 to 5 % by weight, and a heteropolyacid content of from 10 to 900 ppb by weight. Following is a method for producing such a preferred PTMG from THF using a heteropolyacid catalyst. In a

reaction system where water is present in an amount sufficient to form a THF organic phase and an aqueous THF/catalyst phase having a specific gravity of from 1.8 to 2.3, the retention time (V/F) of THF is maintained within the range of from 0.5 to 20 hours, preferably from 0.7 to 15 hours. When the V/F value is smaller than the above-mentioned range, the conversion of THF is likely to become low. On the other hand, when the V/F value is larger than the above-mentioned range, the reaction time is likely to become long. With respect to the motive power (P/V) applied to the liquid in the reactor, the P/V value is maintained at 1.3 kW/m<sup>3</sup> or more, preferably 1.6 W/m<sup>3</sup> or more. When the P/V value is smaller than 1.3 kW/m<sup>3</sup>, the agitation of the reaction system becomes unsatisfactory and the distribution of the diameters of the globules in the reaction system becomes broad. As a result, the molecular weight distribution of the produced PTMG becomes broad and the control of the molecular weight distribution of the PTMG becomes difficult. By appropriately controlling the V/F and P/V values in the above-mentioned method, it is also possible to obtain a PTMG having a number average molecular weight of more than 3,000 and less than or equal to 4,000, and a content of high molecular weight PTMG molecules of more

than 5 % by weight and less than or equal to 10 % by weight.

The heteropolyacid content of the thus obtained PTMG is adjusted to 10 to 900 ppb by weight to obtain the PTMG used in the present invention. The heteropolyacid content can be adjusted by conventional methods, such as a method disclosed in Unexamined Japanese Patent Application Laid-Open Specification No.

61-118420 (corresponding to U.S. Patent No. 4,677,231 and EP 181621), Unexamined Japanese Patent Application Laid-Open Specification No. 61-115934 (corresponding to U.S. Patent No. 4,677,231 and EP 181621), and Unexamined Japanese Patent Application Laid-Open Specification No. 61-123629 (corresponding to U.S. Patent No. 4,677,231 and EP 181621). However, it is preferred that the heteropolyacid content be adjusted by a method which comprises, for example, the following steps ① to ⑥:

① allowing the reaction mixture obtained in the polymerization step to stand still so as to separate the reaction mixture into a reaction-formed aqueous THF/catalyst phase and a reaction-formed THF organic phase containing PTMG, followed by recovering the THF organic phase containing PTMG;

② distilling off a portion of THF in the recov-

ered THF organic phase, to thereby obtain a PTMG concentrate;

③ adding a saturated hydrocarbon having 5 to 10 carbon atoms to the PTMG concentrate so that a catalyst phase (containing a portion of the heteropolyacid dissolved in the PTMG concentrate) and an organic phase is formed, which are separated from each other by phase separation, and subsequently removing the catalyst phase;

④ subjecting the resultant organic phase to a treatment with an activated carbon and the like so as to remove the heteropolyacid dissolved in the organic phase by adsorption;

⑤ distilling off a portion of the monomer (THF) remaining in the organic phase so that a saturated hydrocarbon phase and a PTMG phase are formed; and

⑥ distilling off oligomers and residual organic solvents (such as THF and saturated hydrocarbon) from the obtained PTMG phase using a thin-film evaporator.

Examples of saturated hydrocarbons used in the operation for adjusting the heteropolyacid content of the PTMG include cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, methylcyclopentane, methylcyclohexane, 2-ethylhexane, pentane, hexane, heptane, octane, nonane and decane.



The PTMG used as the component (B) of the polyether polyurethane of the present invention can be in the form of a copolymer, i.e., a copolymer of THF with a monomer other than THF. Examples of comonomers to be copolymerized with THF include 3-methyl-tetrahydrofuran, 1,2-propylene oxide, 3-methyloxetane and the like. There is no particular limitation with respect to the content of comonomer units as long as the comonomer units cause no adverse effects on the properties of the final polyether polyurethane, such as strength, elongation, low-temperature characteristics, flexure resistance, abrasive resistance, elastic recovery, moldability and surface touch. It is preferred that the content of the comonomer units is 20 % by weight or less, more advantageously 10 % by weight or less, based on the weight of PTMG (B).

The chain extender used as the component (C) of the polyether polyurethane of the present invention is at least one chain extender selected from the group consisting of a  $C_2$ - $C_{10}$  polyol having two or more hydroxyl groups and  $C_2$ - $C_{10}$  polyamine having two or more amino groups. The chain extender used in the present invention may also be a compound which functions as a crosslinking agent. Specifically, a chain extender having 3 or more hydroxyl groups or amino groups func-

tions as a crosslinking agent.

The low molecular weight polyol used as the chain extender, is, in a narrow sense, a diol, which has two hydroxyl groups, and such a diol can have a linear or a cyclic configuration. Specific examples of diols include ethylene glycol, 1,3-trimethylene glycol, 1,4-butanediol, 3-methyl-1,4-butanediol, 2,3-butanediol, neopentyl glycol, 1,5-pentamethylene glycol, 2-methylpentamethylene glycol, 3-methylpentamethylene glycol, 1,6-hexamethylene glycol, 1,4-dimethylolcyclohexane, 1,3-dimethylolcyclohexane and 1,2-dimethylolcyclohexane.

The low molecular weight polyol used as the crosslinking agent is a polyol having 3 or more hydroxyl groups, such as an aliphatic polyol and an alicyclic polyol, each having 3 or more hydroxyl groups. Specific examples of polyols having 3 or more hydroxyl groups include trimethylolpropane, glycerin and sorbitol.

The low molecular weight polyamine used as the chain extender, is, in a narrow sense, a diamine, which has two amino groups. Specific examples of diamines include ethylenediamine, hexamethylenediamine, hydrazine, 1,2-propylenediamine, 1,4-butylenediamine, 1,6-hexamethylenediamine, 1,4-cyclohexanediamine, 1,3-cyclohexyldiamine, 4,4'-diaminodiphenylmethane,

4,4'-diaminodicyclohexylmethane, and mixtures thereof.

The low molecular weight polyamine used as the crosslinking agent is a polyamine having 3 or more amino groups. Specific examples of polyamines having 3 or more amino groups include bis(hexamethylene)tri-  
5 amine, 1,3,5-aminomethylcyclohexane and 4-aminomethyloctamethylenediamine.

In the present invention, as the chain extender (C), the above-exemplified low molecular weight polyols  
10 and low molecular weight polyamines can be used individually or in combination.

In addition to the above-mentioned components (A), (B) and (C), optional components, such as a high molecular weight polyol other than PTMG, a prepolymer  
15 having functional terminal groups and a molecular weight modifier, can be used for synthesizing the polyether polyurethane of the present invention.

Examples of high molecular weight polyols other than PTMG include a polyoxyalkylene diol, a polyester  
20 diol, a polycaprolactone diol and a polycarbonate diol.

Examples of prepolymers having functional terminal groups include prepolymers having terminal isocyanate groups which are obtained by modifying the terminals of any of the above-exemplified polyols with a polyisocyanate, and prepolymers obtained by modifying the termi-  
25

nals of any of the above-exemplified polyols with a (meth)acryloyl group or a silyl group.

Examples of molecular weight modifiers include organic amines containing one amino group, such as diethylamine, dimethylamine and dibutylamine.

The polyether polyurethane of the present invention can be produced by conventional urethanation methods, such as a method described in "Poriuretan Jyushi Handobukku (Polyurethane Resin Handbook)", Keiji Iwata ed., Nikkan Kogyo Shimbun Ltd., 1987, and a method described in "Saishin Poriuretan no Kouzou·Bussei to Koukinouka oyobi Ouyoutenkai (Latest report on structures and properties of polyurethane, and improvement in function thereof and development of applications thereof", Technical Information Association, 1999. In general, there are two methods for producing a polyether polyurethane. In the first method, all of the raw materials, such as a polyisocyanate, a high molecular weight polyol and a chain extender, are charged into a reactor at once and a reaction is performed to thereby obtain a polyether polyurethane. In the second method, a first reaction is effected between a polyisocyanate and a high molecular weight polyol to thereby synthesize a prepolymer having terminal isocyanate groups, and then, a second reaction is effected between the synthesized prepolymer and a

chain extender to thereby obtain a polyether polyurethane. Both of the above-mentioned methods can be conducted in the absence or presence of a solvent, and when the reaction is performed in the absence of a solvent, the first method is called "one shot method (one-step method)" and the second method is called "prepolymer method (two-step method)".

As a urethanation catalyst for producing the polyether polyurethane of the present invention, any conventional urethanation catalysts, such as a tin compound and a titanium compound, can be used.

In the present invention, the polyether polyurethane is produced using the PTMG having a number average molecular weight, a molecular weight distribution and a content of high molecular weight PTMG which are within the above-mentioned respective specific ranges, and it is preferred that the PTMG has also a heteropolyacid content within the above-mentioned specific range. Unlike the conventional polyether polyurethanes produced using a polyether diol, such as a conventional PTMG, the polyether polyurethane of the present invention has an excellent balance of physical properties. Specifically, the polyether polyurethane of the present invention exhibits excellent properties, such as high elasticity and elastic recovery, low permanent compression set, excel-

lent low-temperature characteristics and high flexibility, as compared to those of the conventional polyether polyurethanes. Further, the polyether polyurethane of the present invention can be used for forming a coating which has no tack on the surface thereof and is unlikely to suffer discoloration. Thus, the polyether polyurethane of the present invention has high utility.

In another aspect of the present invention, there is provided a urethane prepolymer which comprises (A) a polyisocyanate and (B) a PTMG and which has terminal isocyanate groups. The urethane prepolymer of the present invention has either a structure obtained by bonding polyisocyanates to both terminals of a PTMG molecule so that the resultant molecule has terminal isocyanate groups, or a structure obtained by alternately reacting PTMG with a polyisocyanate so as to form an alternating copolymer of PTMG and a polyisocyanate, which has terminal isocyanate groups.

The polyisocyanate used as component (A) of the urethane prepolymer of the present invention is at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate. There is no limitation with respect to the number of carbon atoms of the polyisocyanate. For ex-

ample, the polyisocyanates, which are mentioned above as examples of polyisocyanate (A) of the polyether polyurethane of the present invention, can also be used for producing the urethane prepolymer. Examples of  
5 such polyisocyanates include aromatic diisocyanates, the aliphatic diisocyanates, and those which are obtained by modifying these diisocyanates with a polyol or the like can be used.

Specific examples of aromatic diisocyanates include 4,4'-diphenylmethane diisocyanate, 2,4-toluene  
10 diisocyanate, 2,6-toluene diisocyanate, 1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1,5-naphthalene diisocyanate and xylylene diisocyanate. As examples of aliphatic diisocyanates, there can be men-  
15 tioned diisocyanates obtained by hydrogenating the aromatic rings of any of the aromatic diisocyanates exemplified above, hexamethylene diisocyanate, isophorone diisocyanate and 4,4-cyclohexyl diisocyanate.

The PTMG used as component (B) of the urethane  
20 prepolymer is a polymeric diol represented by formula (1) above which is obtained by subjecting tetrahydrofuran (THF) to ring-opening polymerization in the presence of a heteropolyacid catalyst. The PTMG used for the urethane prepolymer of the present invention is  
25 the same as that used for the polyether polyurethane of

the present invention. That is, the PTMG used for the urethane prepolymer of the present invention has the following characteristics (1) to (3):

(1) a number average molecular weight of from 500  
5 to 4,000;

(2) a molecular weight distribution of 1.75 or less in terms of the Mw/Mn ratio, wherein Mw represents the weight average molecular weight of PTMG and Mn represents the number average molecular weight of PTMG;  
10 and

(3) a content of high molecular weight PTMG molecules of 10 % by weight or less, wherein the high molecular weight PTMG molecules are defined as PTMG molecules having molecular weights which are at least six  
15 times as large as the number average molecular weight of all PTMG molecules.

In the present invention, it is important that the PTMG has the above-mentioned specific number average molecular weight, specific molecular weight distribution and specific content of high molecular weight PTMG  
20 molecules, and exhibits not only high heat resistance, but also low viscosity. When a urethane prepolymer is synthesized using such a PTMG, and the obtained urethane prepolymer is used for producing a polyether  
25 polyurethane, the produced polyether polyurethane ex-



hibits a good balance of greatly improved properties as compared to that of a polyether polyurethane produced using a conventional PTMG. Illustratively stated, a polyether polyurethane produced using the urethane prepolymer of the present invention exhibits high elasticity and elastic recovery, low permanent compression set and excellent low-temperature characteristics as compared to those of the conventional polyether polyurethane. Further, when such a polyether polyurethane is used for producing a shaped article, there is no tack on the surface of the produced shaped article.

The number average molecular weight of the PTMG used for the urethane prepolymer of the present invention is in the range of from 500 to 4,000, preferably from 750 to 3,500, more preferably from 800 to 3,500, most preferably from 800 to 3,000. When the number average molecular weight of the PTMG is outside the above-mentioned range, as described above in connection with the polyether polyurethane of the present invention, various properties of the final polyether polyurethane produced from the urethane prepolymer of the present invention become unsatisfactory.

The molecular weight distribution of the PTMG used for the urethane prepolymer of the present invention is 1.75 or less, preferably 1.15 to 1.75, more preferably

1.15 to 1.70. When the molecular weight distribution of the PTMG is outside the above-mentioned range, as described above in connection with the polyether polyurethane of the present invention, various properties of the final polyether polyurethane produced from the urethane prepolymer of the present invention become unsatisfactory.

The PTMG used for the urethane prepolymer of the present invention has a content of high molecular weight PTMG molecules of 10 % by weight or less, preferably 2 to 5 % by weight, more preferably 2 to 3.5 % by weight, most preferably 2 to 3 % by weight, based on the total weight of all PTMG molecules. When the content of high molecular weight PTMG molecules is 10 % by weight or less, the PTMG has low viscosity, and a urethane prepolymer produced using such a PTMG also has low viscosity. In addition, such a urethane prepolymer exhibits excellent compatibility with other resins, such as a fluorinated polyol. On the other hand, when the content of the high molecular weight PTMG molecules is more than 10 % by weight, as described above in connection with the polyether polyurethane of the present invention, various properties of the final polyether polyurethane produced from the urethane prepolymer of the present invention become unsatisfactory.

Further, it is preferred that the PTMG used for the urethane prepolymer of the present invention has a heteropolyacid content of from 10 to 900 ppb by weight (1 ppb by weight is  $1 \times 10^{-9}$ ). When the heteropolyacid content of the PTMG is outside the above-mentioned range, as described above in connection with the polyether polyurethane of the present invention, various properties of the final polyether polyurethane produced from the urethane prepolymer of the present invention become unsatisfactory.

The PTMG used for producing the urethane prepolymer can be synthesized in accordance with the above-mentioned methods for synthesizing PTMG.

As in the case of the PTMG used for the polyether polyurethane of the present invention, the PTMG (B) used for the urethane prepolymer can be in the form of a copolymer of THF with a monomer other than THF.

The urethane prepolymer of the present invention can be synthesized by the conventional methods, such as a method described in "Poriuretan Jyushi Handobukku (Polyurethane Resin Handbook)", Keiji Iwata ed., Nikkan Kogyo Shimbun Ltd., 1987. For example, a urethane prepolymer having terminal isocyanate groups can be obtained by modifying a PTMG with a polyisocyanate.

The terminal isocyanate groups of the urethane

prepolymer of the present invention can be partly or wholly modified so as to have at least one functional group other than an isocyanate group, wherein the functional group is introduced into the terminal isocyanate groups by addition. The functional group introduced into the terminal isocyanate group is a functional group selected from the group consisting of a (meth)acryloyl group and a silyl group. By such modification of the terminal isocyanate groups, it is possible to obtain urethane prepolymers suitable for use in various applications. For example, a urethane prepolymer suitable as a raw material for a photosensitive resin can be obtained by introducing carbon-carbon double bond-containing groups into the terminals of a urethane prepolymer. For example, a carbon-carbon double bond-containing groups can be introduced into the terminals of a urethane prepolymer by reacting the urethane prepolymer having terminal isocyanate groups with a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, itaconic acid, an acrylate-modified polymeric polyol, a methacrylate-modified polymeric polyol. Specifically, as examples of methods for introducing carbon-carbon double bond-containing terminal groups, there can be mentioned a method in which a urethane prepolymer having terminal isocyanate groups is reacted with an

acrylate, such as hydroxymethyl acrylate, so that the terminal isocyanate groups are modified to have an acryloyloxy group; a method in which a urethane prepolymer having terminal isocyanate groups is reacted  
5 with a methacrylate, such as hydroxymethyl methacrylate, so that the terminal isocyanate groups are modified to have a methacryloyloxy group; and a method in which a urethane prepolymer having terminal isocyanate groups is reacted with a hydroxyl group-containing poly-  
10 siloxane, so that the terminal isocyanate groups are modified to have a silyl group.

The urethane prepolymer of the present invention can be widely used as a precursor of a polyether polyurethane. Conventional methods can be used as a ure-  
15 thanation method for obtaining a polyether polyurethane from the urethane prepolymer. Specifically, a polyether polyurethane can be obtained by reacting the urethane prepolymer with a chain extender.

When a polyether polyurethane is synthesized from  
20 the urethane prepolymer of the present invention, optional components, such as a polyisocyanate having 2 or more isocyanate groups, a polymeric polyol other than PTMG, a prepolymer having functional terminal groups, a chain extender and a molecular weight modifier, can be  
25 used in combination with the urethane prepolymer.

Examples of polyisocyanates having 2 or more isocyanate groups which can be used in combination with the urethane prepolymer of the present invention include an aromatic diisocyanate, an aliphatic diisocyanate, and those which are obtained by modifying these diisocyanates with a polyol or the like.

Specific examples of polyisocyanates include aromatic diisocyanates, such as 4,4'-diphenylmethane diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1,5-naphthalene diisocyanate and xylylene diisocyanate; aliphatic diisocyanates, such as diisocyanates obtained by hydrogenating the aromatic rings of any of the aromatic diisocyanates exemplified above, hexamethylene diisocyanate, isophorone diisocyanate, and 4,4-cyclohexyl diisocyanate; and the above-mentioned modified polyisocyanates, such as isocyanurate type polyisocyanate, and blocked polyisocyanates obtained by modifying polyisocyanates with an oxime compound and the like.

With respect to other optional components, such as the high molecular weight polyols other than PTMG, prepolymers having functional terminal groups, chain extenders and molecular weight modifiers, those which can be used for producing the polyether polyurethane of the

present invention can also be used.

As an urethanation catalyst used for producing a polyether polyurethane from the urethane prepolymer of the present invention, those which can be used for producing the polyether polyurethane of the present invention can also be used.

In the present invention, the urethane prepolymer is produced using the PTMG which has a number average molecular weight, a molecular weight distribution and a content of high molecular weight PTMG molecules which are within the above-mentioned respective specific ranges, and it is preferred that the PTMG has also a heteropolyacid content within the above-mentioned specific range. Unlike the conventional polyether polyurethane produced using a polyether diol, such as a conventional PTMG, a polyether polyurethane produced using the urethane prepolymer of the present invention has an excellent balance of physical properties. Specifically, such a polyether polyurethane exhibits excellent properties, such as high elasticity and elastic recovery, low permanent compression set, excellent low-temperature characteristics and high flexibility, as compared to those of the conventional polyether polyurethanes. Further, such a polyether polyurethane can be used for forming a coating which has no tack on the

surface thereof and is unlikely to suffer discoloration. Thus, the urethane prepolymer of the present invention has high utility. Further, when a composition, such as a coating composition, is prepared using the urethane prepolymer of the present invention, the prepared composition also exhibits excellent properties (such as excellent fluidity before curing, excellent drying characteristic, and capability of forming a coating having no surface tack).

By utilizing the above-mentioned excellent balance of various properties, the polyether polyurethane and urethane prepolymer of the present invention can be used in the various application fields mentioned below.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can be used as a material for a flexible foam. For example, the flexible foam can be used for producing automobile parts, such as a cushion, a ceiling material, an inner material of a door trim, a padding, a sun visor, a cushioning for a floor, a waterproofing material for a car cooler, a damper and an air sealing material. The flexible foam can also be used for producing beddings, such as a mattress, a Japanese futon (bed quilt), a ma-



tress for a Japanese kotatsu (foot warmer), a pillow and the like; sponges for dish washing; sponges for washing bodies; powder puffs; inner linings of shoes; slippers; and clothes. The flexible foam can also be  
5 used for producing parts of electric and electronic equipments, such as a filter of an air conditioner, a sound absorption material, a heat insulation material, a material for producing an edge of a speaker, and a sound absorption material of a printer. Further, in  
10 the fields related to packings, the flexible foam can be used as a cushioning material, a packaging material, and an electrical conductive packaging material. In addition, the flexible foam can be used for producing various articles used in the fields related to clinical  
15 equipments; sealing materials, sound absorption materials and heat insulation materials which are used for civil engineering and construction; and highly air permeable foams for hydroponics.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the  
20 urethane prepolymer of the present invention can also be used as a material for a flexible molded foam. For example, the flexible molded foam can be used for producing a cushioning of an automobile, a seat of an  
25 automobile, an underlayment of a carpet, a packing for

a carpet and a floor material for an automobile.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also  
5 be used as a material for a semirigid foam. For example, the semirigid foam can be used for producing interior automobile trims, such as a dashboard, a headrest, an armrest, a kneepad, a pillar pad, a console box, a sun visor, a floor mat, a horn pad, an ashtray, a handle wheel and a door panel; and exterior automobile  
10 trims, such as a bumper, a fender and a sound insulation material for a tire housing.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also  
15 be used as a material for a rigid foam. For example, the rigid foam can be used for producing parts used in the fields related to ocean engineering, such as a heat insulation material for a pantry, a freezer, a container and a tank of a ship; a core material of an FRP (fiber reinforced plastic) board; a floatation material  
20 of a lifeboat; a floating dock for a target boat and a large ship; a buoy and a float. In addition, the rigid foam can also be used for producing a heat insulation  
25 material for a pantry, a freezer, a container and a

tank, which are attached to an automobile; and a heat insulation material for a ceiling of vehicles, such as a train. Further, in industrial plants, the rigid foam can also be used for a heat insulation material of tanks and pipes, a lagging material or low-temperature insulation material of a tank, a cover for heat insulation, a lid of a tank and the like. The rigid foam can also be used for a heat insulation material for a household refrigerator or air conditioner, a heat insulation material for a showcase type storage, a vending machine, a water heater, a hot well and the like. In addition, the rigid foam can also be used as construction materials, such as a core material of a panel; a siding material; a heat insulation material for a bathtub, a freezing storage, a refrigerating storage, an isothermal storage, an agricultural storage and a shed; a heat insulation material for a central heating; a heat insulation material for a roof; a material for preventing house dew condensation (which is, for example, used for a ceiling, an inner wall or used under the floor); a heat insulation material for the roadbed and an antivibration material. In the field related to furnitures, interior and the like, the rigid foam can be used as a material for a core material of a chair, a door panel, decorations and craft works, a plaything, a

cool box, a canteen, a teaching material, a three dimensional map, a shaping material, a heat insulation material of a sash, a core material for a ski, a housing, a wrapping and the like.

5           The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also be used as a material for flexible RIM (Reaction Injection Molding) articles. Examples of the flexible RIM  
10 articles include automobile parts, such as a bumper, a facer, a fender, an air spoiler, a door panel, a rear, lower quarter panel, a front hood, a cover of a headlamp, a roof, a lid of a rear deck, a rear, upper quarter panel, a steering wheel, a crush pad, a head-  
15 rest, a console box and a pillar. Further examples of the flexible RIM articles include a shoe sole and an armrest of a furniture.

          The polyether polyurethane of the present invention and a polyether polyurethane produced from the  
20 urethane prepolymer of the present invention can also be used as a material for rigid RIM articles. Examples of the rigid RIM articles include electrical equipments, such as cabinets of a television, a radio and a stereo; a drainage receiver of an air conditioner; a speaker  
25 cabinet; a casing of a player; a screen; a door frame

of a refrigerator; a center desk of a telephone; a casing of a telephone exchanger; a switch box; a covering for an input port of a cable; and a box for branched cables. Examples of the rigid RIM articles used for office appliances include a desk, a chair, a casing of a cabinet, a housing of a copying machine, a housing of a computer, a housing of a word processor and a box for medicines. Examples of the rigid RIM articles used in the fields related to vehicles and transport equipments include a container for meals served on airplanes, a cabinet of a car air conditioner, a back of an airplane seat, a casing of a battery, parts of agricultural appliances and construction appliances, a pallet, a door of an automobile, a cover of an equipment, and a filter. Further examples of the rigid RIM articles include sports articles and leisure articles, such as a core material of skis, an inner sole, a racket, a rudder of a yacht, an oar of a boat, a sleigh, a sleigh with rollers, a game machine, a musical instrument and a movable comb hive; and the building materials and daily commodities, such as a window frame, a frame of a lighting window, an exhaust vent, a drainage, a washstand and a dressing table, a frame of a mirror, a fake wood carving, an imitation of an old wood, a chair, a desk, a fence, a coat hanger, a

kitchen unit and a vase.

The polyether polyurethane and urethane prepolymer of the present invention can also be used for a cast polyurethane elastomer. For example, the cast polyurethane elastomer can be used as a material for rolls, such as a pressure roll, a paper-making roll, a roll for office appliances and a platen roll; solid tires or casters of a fork lift truck, a vehicle of a new-tram, a cart and a truck; industrial products, such as an idler roller of a conveyor belt, a guide roll, a pulley, a lining of a steel tube, a rubber screen for an ore, a gear, a connection ring, a liner, an impeller of a pump, a cyclone cone and a cyclone liner. Further, the cast polyurethane elastomer can also be used for producing a belt of an office automation machine, a roll for feeding paper, a squeegee, a cleaning blade of a copying machine, a snowplow, a toothed belt, a surf roller and the like.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also be used for the thermoplastic elastomer. For example, in the fields related to food industries and clinical equipments, the thermoplastic elastomer can be used as a material for tubes and hoses for a pneumatic instru-

ment, a coating apparatus, an analytical instrument, a physicochemical instrument, a metering pump, a water treatment apparatus and an industrial robot; spiral tubes; fire hoses and the like. The thermoplastic elastomer can also be used for producing belts, such as a round belt, a V-belt and a flat belt which are used in various driving mechanisms, spinning machines, packaging machines, printing machines and the like. Further, examples of injection molded articles of the thermoplastic elastomer include heel tops of shoes and soles of sports shoes; machine parts, such as a coupling, a packing, a ball joint, a bushing, a gear and a roll; sports articles; leisure articles; and belts of digital watches. Examples of automobile parts produced from the thermoplastic elastomer include an oil stopper, a gearbox, a spacer, a chassis part, an interior trim and a substitute for a tire chain. In addition, a film for a keyboard, a covering for a keyboard, a film for an automobile sheet, a curled cord, a cable sheath, a bellows, a conveyance belt, a flexible container, a binder, a synthetic leather, a dipped article, an adhesive and the like can be produced using the thermoplastic elastomer.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the

urethane prepolymer of the present invention can also be used for a kneaded elastomer. For example, the kneaded elastomer can be used as a material for a belt for moving small articles, parts of a small article, an O-ring, a bushing, a coupling, an oil seal, a dust cover of an automobile, a stopper and an impeller. The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can be used for a sprayed elastomer and a low-temperature curing elastomer which can be used for producing linings of a bed of a truck, linings of a hopper of a mixermobile, coatings of a floor, tracks used for athletic competitions, gaskets of a large pipe, sealing materials and the like.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can be used as a material for a solvent type two-pack coating composition. Such a solvent type two-pack coating composition can be used on wooden articles, such as a musical instrument, a household Buddhist altar, a furniture, a decorating plywood and a sports article. The polyether polyurethane can also be used as a material for producing a tar epoxy urethane for repairing automobiles. The polyether polyurethane can also be used



as a material for a non-solvent type two-pack coating composition, such as a tar urethane.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also be used as a component for coating compositions, such as a moisture curing type one-pack coating composition; a solvent type coating composition containing a blocked isocyanate; an aqueous coating composition containing a blocked isocyanate; a powdery coating composition; a urethane alkyd resin coating composition; a urethane-modified synthetic resin coating composition and an UV curing type coating composition, and specific examples of such coating compositions include a coating composition for a plastic bumper; a strippable paint; a coating agent for a magnetic tape; an overprint varnish for a floor tile, a floor material, a paper and a vinyl film with wood grain printing; a varnish for wood; a coil coating for highly processed materials; a protective coating for optical fibers; a solder resist; a top coat for metal printing; a base coat for deposition; a white coating for cans used for food.

The polyether polyurethane and the urethane prepolymer of the present invention have low viscosity, and when a two-pack coating composition is produced using

the polyether polyurethane or the urethane prepolymer, the produced two-pack coating composition exhibits low viscosity even immediately after mixing the two components of the two-pack coating composition. Thus, the  
5 polyether polyurethane and the urethane prepolymer of the present invention are suitable as materials for producing a high solid type coating.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the  
10 urethane prepolymer of the present invention can also be used as an adhesive in the fields of a package for food, a shoe, a footwear, a binder for magnetic tapes, a decorative paper, a wood, a structural material and the like. Further, the polyurethane can also be used  
15 as a component for an adhesive for use at very low temperatures and also as a component for a hot melt.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the  
20 urethane prepolymer of the present invention can be used as a binder for a magnetic recording medium, an ink, a casting, a calcined brick, a grout, a microcapsule, a granular fertilizer, a granular pesticide, a polymer cement mortar, a resin mortar, a rubber chip, a recycled foam, a sizing agent for glass fibers and the  
25 like.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also be used as a component of fiber processing agents to be used for an anti-shrink treatment, a crease resistant finish, a water repellency-imparting treatment and the like.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also be used as a sealant or a caulking for a concreted wall, an induced joint, a gap around a sash frame, a wall type PC joint, an ALC joint, a joint of boards, a sealant for a composite glass, a sealant for a heat insulation sash, a sealant for an automobile and the like.

The polyether polyurethane of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention can also be used as a material for clinical equipments. For example, the polyether polyurethane can be used as a blood compatible material for tubes, catheters, artificial hearts, artificial vessels, artificial valves and the like, and as a disposable material for catheters, tubes, bags and a potting material of an artificial kidney.

After modifying the terminals of the urethane prepolymer, the urethane prepolymer of the present invention can be used as a raw material for an UV curing type coating composition, an electron radiation curing type coating composition, a photosensitive resin composition for flexographic printing plate, a photo-setting type coating composition for optical fibers and the like.

The uses of the polyether polyurethane of the present invention, the urethane prepolymer of the present invention and a polyether polyurethane produced from the urethane prepolymer of the present invention are exemplified above, but they should not be construed as limiting the uses of the products of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinbelow, the present invention will be described in more detail with reference to the following Reference Examples, Examples and Comparative Examples, but they should not be construed as limiting the scope of the present invention.

Polyoxytetramethylene glycols (hereinafter, polyoxytetramethylene glycol is frequently referred to as "PTMG") used in the Examples and the Comparative Examples were synthesized in accordance with the following Reference Examples.

Reference Example 1

PTMG was produced using the production system shown in Fig. 1.

First, a heteropolyacid catalyst solution for use as a polymerization catalyst was produced as follows. A 2-liter reaction vessel was prepared, which is provided with a 3-way cock having three respective ends, wherein each end has attached thereto a condenser and an eggplant type flask for collecting and storing a distillate produced by the condenser, so that the contents of the reaction vessel can be distilled. The thus prepared reaction vessel was used for producing a

heteropolyacid catalyst solution. 1 liter of tetrahydrofuran (THF) and 600 g of silicotungstic acid dodecahydrate were introduced into the reaction vessel in this order, and stirred at 60 °C, while continuously removing an azeotropic vapor of water and THF from the reaction vessel. The specific gravity of a solution being formed in the reaction vessel was periodically measured while feeding THF to the reaction vessel every 10 minutes so as to compensate for the total amount of water and THF removed from the reaction vessel. When the specific gravity of the solution became 2.07, the reaction was terminated to thereby obtain a catalyst solution having a specific gravity of 2.1, namely, a solution of a heteropolyacid catalyst in a THF/water mixture.

Next, polyoxytetramethylene glycol was produced by the following operation. Reactor 2 having a capacity of 500 ml was equipped with stirrer 1 and a reflux condenser. 180 ml of the above-obtained catalyst solution (CS) was charged into reactor 2 and 240 ml of THF (monomer) was added thereto to thereby obtain a reaction system comprised of a THF organic phase and an aqueous THF/catalyst phase. The obtained reaction system was stirred at 60 °C while maintaining the motive power (P/V) applied to the liquid per unit volume of

the reactor at  $1.95 \text{ kW/m}^3$  and while feeding THF to reactor 2 at a rate of 64 ml/hour, to thereby obtain a polymerization reaction mixture comprising a reaction-formed THF organic phase containing a polyoxytetramethylene glycol and a reaction-formed aqueous THF/catalyst phase. The retention time (V/F) of THF in reactor 2 was 6.6 hours. During the reaction, water was fed to reactor 2 from water feeding tank 3 so as to maintain the specific gravity of the aqueous THF/catalyst phase at 2.07. A part of the polymerization reaction mixture was transferred into first, phase-separation vessel 4, thereby separating the reaction mixture into two phases, namely an upper reaction-formed THF organic phase containing a polyoxytetramethylene glycol and a lower reaction-formed aqueous THF/catalyst phase. The upper phase was withdrawn from first, phase-separation vessel 4 at a rate which is the same as the rate of the feeding of THF, while the lower reaction-formed aqueous THF/catalyst phase (CP) was recycled to reactor 2.

The upper phase withdrawn from first, phase-separation vessel 4 (i.e., the reaction-formed THF organic phase containing polyoxytetramethylene glycol) was fed into distillation vessel 5 for removing unreacted THF. The THF concentration of the organic phase

was adjusted to 45 to 50 % by weight, thereby obtaining a polyoxytetramethylene glycol concentrate.

The above-mentioned operation for obtaining a polyoxytetramethylene glycol was continuously performed for 50 hours. 100 g of the polyoxytetramethylene glycol concentrate produced during the stable operation of the reactor was subjected to the following operations for adjusting the heteropolyacid content of the polyoxytetramethylene glycol.

100 g of the polyoxytetramethylene glycol concentrate was fed into second, phase-separation vessel 6. 120 g of n-octane (solvent, S) was added to second, phase-separation vessel 6 and stirred for 5 minutes at room temperature, thereby obtaining a mixture. The obtained mixture was allowed to stand still for approximately 5 minutes, so that the mixture was separated into a lower aqueous THF/heteropolyacid catalyst phase (CP) and an upper organic phase. 200 g of the upper organic phase which is a solution containing polyoxytetramethylene glycol was placed in a 500 ml eggplant type flask which was warmed in a water bath maintained at 50 °C. Subsequently, the solution was applied to adsorption column 7 at a rate of 100 g/hour using a pump. Adsorption column 7 was a column packed with 1 kg of an activated carbon (AC) and the column had an



outer jacket in which water heated to 45 °C was circulated so as to maintain the inner temperature of adsorption column 7 at 40 °C or higher.

5 An eluate (approximately 200 g) obtained from adsorption column 7 was placed in a 300 ml eggplant type flask heated in an oil bath maintained at 100 °C. The eggplant type flask was equipped with Oldershaw distillation column 8 (number of theoretical plates: 10). The eluate in the eggplant type flask was subjected to  
10 distillation under atmospheric pressure with stirring to thereby remove THF in the eluate. The residual solution in the flask was transferred to a 300 ml separation funnel used as third, phase-separation vessel 9. In third, phase-separation vessel 9, the solution was  
15 allowed to separate into two phases, namely a phase containing polyoxytetramethylene glycol as a main component and a phase containing n-octane (S) as a main component. The lower phase (approximately 30 g) containing polyoxytetramethylene glycol was taken out from  
20 third, phase-separation vessel 9 and subjected to vacuum distillation in vacuum distillation vessel 10 for 20 minutes at 100 °C under a reduced pressure of not more than 0.1 Torr. Low-boiling point substances (LBPS), such as n-octane, THF and oligomers, were dis-  
25 tilled off to thereby obtain PTMG (A). The obtained

PTMG (A) was approximately 23 g.

The obtained PTMG (A) had a number average molecular weight ( $M_n$ ) of 1840, a molecular weight distribution ( $M_w/M_n$ ) of 1.60, and a content of high molecular weight PTMG molecules which are at least six times as large as the number average molecular weight of all PTMG molecules (hereinafter, simply referred to as "content of high molecular weight PTMG molecules") of 2.29 % by weight. These values were determined by gel permeation chromatography (GPC) under the conditions mentioned below.

A chromatogram of PTMG (A) which shows the molecular weight distribution of PTMG (A) is shown in Fig. 2. In Fig. 2, the abscissa shows the logarithm ( $\log$ ) of the molecular weight; the ordinate shows the weight % of component PTMG molecule, based on the total weight of all PTMG molecules; and the intersection of the vertical straight broken line and the abscissa shows the logarithm of the number average molecular weight. The area of a hatched portion shows the amount of the PTMG molecules having molecular weights (11,040 or more;  $\log$  (molecular weight) = 4.04 or more), which are at least six times as large as the number average molecular weight ( $M_n = 1,840$ ;  $\log M_n = 3.26$ ) of all PTMG molecules. The ratio of the area of the hatched portion to

the total area of the peak is 2.29 %.

The heteropolyacid content of the obtained PTMG was determined by ICP-Mass spectrometry in terms of the tungsten (W) content, and found to be 270 ppb by weight.

5 In the present invention, the terminal titration method, GPC, ICP-Mass spectrometry and determination of E-type viscosity were individually conducted under the following conditions.

10 Terminal titration method

The terminal titration method was conducted in accordance with the method described at page 353 of "Bunseki Kagaku Benran (Handbook of Analytical Chemistry)", Revised 3rd edition, Japanese Society of Analytical  
15 Chemistry ed., in which anhydrous acetic acid and pyridine are used.

Conditions for GPC analysis

GPC apparatus: Shodex GPC system-11 (manufactured and  
20 sold by Showa Denko K.K., Japan)

Column: Shodex OH pack (manufactured and sold by Showa Denko K. K., Japan):

SB 806 M (2 columns)

SB 802.5 (1 column)

25 Detector: Differential refractometer

Column temperature: 60 °C

Carrier (eluent): 0.02 mol/liter LiBr solution of  
dimethylacetamide

Flow rate of carrier: 1.0 ml/min

5 Sample: 100 µl of 0.8% PTMG solution in the carrier

Molecular weight standards: PTMG, Mn = 547,000 (Mw/Mn

= 1.35), Mn = 283,000 (Mw/Mn = 1.08), Mn = 99,000

(Mw/Mn = 1.08), Mn = 67,000 (Mw/Mn = 1.04), Mn =

35,500 (Mw/Mn = 1.06), Mn = 15,000 (Mw/Mn = 1.09),

10 Mn = 6,700 (Mw/Mn = 1.13), Mn = 2,170 (Mw/Mn = 1.12),

Mn = 1,300 (Mw/Mn = 1.12), Mn = 650 (Mw/Mn = 1.18),

and THF monomer.

#### Conditions for ICP-Mass Spectrometry

15 Approximately 5 g of a sample PTMG was heated in a  
quartz crucible to thereby calcine the sample PTMG. To  
the calcined PTMG was added 2 ml of 35 % hydrochloric  
acid solution. Then, the resultant mixture was heated  
to decompose the calcined PTMG. To the decomposed PTMG  
20 was added 0.1 ml of an aqueous 1 ppm indium (In) solu-  
tion as an internal standard and then added water in an  
amount such that the final volume of the resultant so-  
lution became 25 ml, to thereby obtain a sample PTMG  
solution. The obtained sample PTMG solution was sub-  
25 jected to ICP-Mass spectrometry using PQΩ-type ICP-MS

(manufactured and sold by VG Elemental, England). The heteropolyacid content of PTMG was determined as the tungsten content of the PTMG using a calibration curve for tungsten (W).

5           The calibration curve used for determining the tungsten content was prepared using standard tungsten solutions which contained tungsten in various concentrations (5 to 10,000 ppb by weight). The standard tungsten solutions were prepared by adding 0.1 ml of an  
10           aqueous 1 ppm indium (In) solution as an internal standard to each of tungsten solutions (in 35 % hydrochloric acid solution) having various concentrations, and adding water thereto so that the final volume of the resultant solution becomes 25 ml.

15

#### E-type viscosity

Apparatuses: E-type viscometer (Controller E2, manufactured and sold by TOKIMEC, Japan) and circulating constant-temperature bath  
20           (VCH-4, manufactured and sold by TOKIMEC, Japan)

Temperature: 40 °C

Revolution of rotor: 20 rpm

25           Reference Example 2

PTMG (B) was produced in substantially the same manner as in Reference Example 1, except that 80 ml of a phosphomolybdic acid solution having a specific gravity of 1.8 was used as a catalyst solution, the initial amount of THF charged in the reactor was 340 ml, the rate of feeding of THF was 42 ml/hr, the V/F value of THF in the reactor was 10 hours, and the P/V value was 2.3 kW/m<sup>3</sup>.

The produced PTMG (B) had a number average molecular weight of 870, a molecular weight distribution of 1.70, a content of high molecular weight PTMG molecules of 4.35 % by weight, and a heteropolyacid content of 320 ppb by weight.

Besides the PTMG's produced by the Reference Examples above, the below-mentioned commercially available PTMG's were purchased and used in the Comparative Examples. The number average molecular weights, the molecular weight distributions, the contents of high molecular weight PTMG molecules, the heteropolyacid contents and the viscosities of the commercially available PTMG's were determined in the above-mentioned manner, and are shown in Table 1.

PTMG (E): "Polytetramethylene glycol PTG 2000", manu-

factured and sold by Hodogaya Chemical Co.,  
Ltd., Japan

5 PTMG (F): "Polytetramethylene glycol PTG 1000", manu-  
factured and sold by Hodogaya Chemical Co.,  
Ltd., Japan

PTMG (G): Polytetramethylene ether glycol 1000, manu-  
factured and sold by BASF AG, Germany

PTMG (K): Polytetramethylene ether glycol 2000, manu-  
factured and sold by BASF AG, Germany

10 PTMG (L): Polytetramethylene ether glycol 2000, manu-  
factured and sold by Du Pont, USA

PTMG (M): Polytetramethylene ether glycol 2000, manu-  
factured and sold by Mitsubishi Chemical  
Corporation, Japan

15 PTMG (P): Polytetramethylene ether glycol 1000, manu-  
factured and sold by Mitsubishi Chemical  
Corporation, Japan

76

[illegible]



In the Examples and the Comparative Examples, various properties of the polyether polyurethane and the urethane prepolymer produced were evaluated and measured by the following methods.

5

① NCO group content

The isocyanate (NCO) group content (% by weight) of the urethane prepolymer was measured by the amine equivalent method. Specifically, an excess amount of  
10 n-dibutylamine was added to the urethane prepolymer, to thereby completely react the isocyanate groups contained in the urethane prepolymer with n-dibutylamine. After the termination of the reaction, the amount of unreacted n-dibutylamine contained in the reaction mixture  
15 was determined by back titration using hydrochloric acid/methanol for determining the NCO group content of the urethane prepolymer.

② HDI concentration

20 The hexamethylene diisocyanate (HDI) concentration (% by weight) of the urethane prepolymer is the ratio of unreacted HDI remaining in the urethane prepolymer. The HDI content was measured by gas chromatography under the following conditions:

25 Apparatus: GC-8AFID (manufactured and sold by

Shimadzu Corporation, Japan);

Column: 1 m glass packed column;

Filler: Silicon OV-17;

Column temperature: 120 °C;

5 Carrier gas: 40 to 60 ml/min of nitrogen;

Injection temperature: 170 °C;

FID (detector) temperature: 170 °C;

Amount of the injected sample: 0.8 µl;

Internal standard: nitrobenzene; and

10 Sample: 10 % urethane prepolymer solution in  
ethyl acetate.

### ③ Drying characteristic

The drying characteristic was evaluated in accordance with JIS K5400 by touching the test specimens  
15 with fingers. The test specimens which were relatively  
dry as compared to other test specimens were evaluated  
as having good drying characteristic.

### 20 ④ Hardness

'A' hardness was measured in accordance with JIS  
K6301.

### ⑤ Elongation at break and tensile strength at break

25 Elongation at break and tensile strength at break

were measured in accordance with JIS K6301 (using a dumbbell No. 3 prescribed therein) or JIS K6254.

⑥ Dunlop impact resilience

5           Dunlop impact resilience was measured in accordance with BS 903 at room temperature.

⑦ Viscoelasticity index

10           The viscoelasticity index was obtained in terms of the value of  $2C_1$  which is the primary approximate aspect of the contributions of chemical crosslinkages and permanent entanglements of polyurethane molecules to the elasticity of a polyurethane. The  $2C_1$  value was calculated in accordance with the Mooney-Rivlin formula  
15 below:

$$\sigma = 2C_1 (\alpha - \alpha^{-2}) + 2C_2 (1 - \alpha^{-3})$$

          wherein  $\alpha$  represents the elongation ratio,  $\sigma$  represents the normal stress, and  $2C_2$  represents the contribution of the physical  
20 crosslinkage to the elasticity of the polyether polyurethane.

          Specifically, the elongation ( $\epsilon$ ) and normal stress ( $\sigma$ , the load per initial crosssectional area) of the polyether polyurethane were measured in accordance with

JIS K6254 (wherein a polyether polyurethane strip having a width of 5 mm and a thickness of 2 mm was used as a test specimen, the distance between chucks was 30 mm and the rate of elongation was 10 mm/min (33.33 %/min)),  
5 thereby obtaining a graph shown in Fig. 3. Using the obtained graph, the value for  $\sigma$  was determined from the ordinate of the graph and the value for  $\alpha$  was determined in accordance with the following relationship:  $\alpha = \epsilon + 1$  by using the  $\epsilon$  value obtained from the abscissa  
10 of the graph. Using elongation ratio  $\alpha$  and normal stress  $\sigma$  obtained above,  $\sigma/(\alpha - \alpha^{-2})$  values were plotted against  $1/\alpha$  values, and from intercept of the plotted curve was obtained the  $2C_1$  value.

15 ⑧ Storage elastic modulus and loss elastic modulus (dynamic viscoelasticity)

Using a test specimen having a length of 15 mm, a width of 4 mm and a thickness of 2 mm, storage elastic modulus ( $E'$ ) and loss elastic modulus ( $E''$ ) of the  
20 polyether polyurethane were measured using a measuring apparatus (Direct-reading type RHEOVIBRON (DDV-IIC type), manufactured and sold by ORIENTEC CORPORATION, Japan) under conditions wherein the frequency was 110 Hz and the temperature was -150 °C to 250 °C. In addition,  
25 the dissipation factor ( $\tan \delta$ , a ratio of loss

elastic modulus to storage elastic modulus) was determined from the obtained data.

⑨ Observation under polarization microscope

5           An ultra thin piece of polyether polyurethane was cut out from a sheet of the polyether polyurethane, and the piece of polyether polyurethane was observed under a polarization microscope (OPTIPHOTO2-POL, manufactured and sold by NIKON CORP., Japan) using crossed Nicols.  
10          Further, a sensible color plate was inserted into the polarization microscope, and the orientation of spherulites of the polyether polyurethane was observed.

Example 1

15           A 2-liter flask provided with a thermometer, a refrigerator and a stirrer was charged with 616 g of hexamethylene diisocyanate (HDI) and 450 g of PTMG (A), thereby obtaining a mixture (NCO group/OH group molar ratio of the obtained mixture = 15). A reaction was  
20          performed at 100 °C for 1 hour with stirring. The reaction mixture was subjected to distillation at 160 °C under a vacuum degree of 0.2 mHg by means of a thin film evaporator to remove unreacted HDI from the reaction mixture, thereby obtaining 525 g of urethane prepolymer PA. The obtained urethane prepolymer PA had an  
25

NCO group content of 3.8 % by weight and an HDI concentration of 0.1 % by weight. When urethane prepolymer PA was observed by visual observation, the fluidity of urethane prepolymer PA was excellent. The amounts of raw materials charged to the flask for preparing urethane prepolymer PA and the properties of urethane prepolymer PA are shown in Table 2.

Urethane prepolymer PPCL was produced using polycaprolactone polyol (Mn: 850, number of functional groups: 3) (Praccel 308, manufactured and sold by Daicel Chemical Industries, Japan) and HDI in the same manner as mentioned above. Polycaprolactone polyol and HDI were used in the amounts shown in Table 2 so that the NCO group/OH group molar ratio of the resultant mixture became 15. The fluidity of urethane prepolymer PPCL was inferior to that of urethane prepolymer PA. The polymerizing conditions for producing urethane prepolymer PPCL and the properties of urethane prepolymer PPCL are shown in Table 2.

7.08 parts by weight of urethane prepolymer PA and 7.08 parts by weight of urethane prepolymer PPCL were mixed together, thereby obtaining a curing agent for a coating composition. To the obtained curing agent was added 25 parts by weight of an acryl polyol (OH value: 50 mg KOH/g, Tg: 70 °C) (ACLYDIC A801, manufactured and

sold by DAINIPPON INK & CHEMICALS, INC., Japan) as a main component of the coating composition, and the viscosity of the resultant mixture was adjusted to a value of 15 seconds in terms of the time measured using Ford viscosity cup No. 4, by diluting the mixture with toluene, to thereby obtain a coating composition. The obtained coating composition was spray coated on a polypropylene substrate having a length of 15 cm and a width of 15 cm, and the coating was dried at 20 °C at a relative humidity of 60 % for 1 week. The coating was removed from the substrate to thereby obtain a sheet having a thickness of 100 µm. Elongation at break and tensile strength at break of the obtained sheet were measured in accordance with JIS K6301 at -30 °C (wherein a strip having a width of 10 mm and a thickness of 100 µm was prepared from the sheet and used as a test specimen, the distance between chucks was 50 mm and the rate of elongation was 100 %/min). The sheet exhibited excellent properties with respect to both the elongation at break and tensile strength at break, that is, the elongation at break of 145 % and the tensile strength at break of 122 kgf/cm<sup>2</sup>. The drying characteristic of the sheet was also excellent. Further, the sheet had excellent flexibility. The composition of the coating composition is shown in Table 3 together

with the properties of the coating.

Further, the above-prepared curing agent was mixed with a fluorine type polyol (LUMIFLON 2000, manufactured and sold by Asahi Glass Co., Ltd., Japan) which is used as a main component for a coating composition, and a film was prepared using the resultant mixture. The prepared film was visually observed, and it was found that the film was not turbid. From the above result, it was understood that the curing agent prepared using the urethane prepolymer of the present invention had excellent compatibility with a fluorine type polyol.

#### Example 2

Urethane prepolymer PB was produced in substantially the same manner as in Example 1, except that PTMG (B) having a smaller Mn than that of PTMG (A) was used instead of PTMG (A), and PTMG (B) and HDI were used in amounts shown in Table 2 so that the NCO group/OH group molar ratio of a PTMG (B)/HDI mixture became 15. The properties of urethane prepolymer PB are shown in Table 2.

Using urethane prepolymer PB, a coating composition was produced in substantially the same manner as in Example 1, except that the amounts of the components for the composition were changed as shown in Table 3.



A coating was formed and the properties of the formed coating were evaluated in the same manner as in Example 1.

Further, with respect to the curing agent prepared using the urethane prepolymer (prepolymer PB) of the present invention, the compatibility of the curing agent with a fluorine type polyol was evaluated in the same manner as in Example 1. The results are shown in Table 3.

#### Comparative Example 1

Urethane prepolymer PE was produced in substantially the same manner as in Example 1, except that PTMG (E) (commercially available PTMG) having an Mn close to that of PTMG (A) was used instead of PTMG (A), and PTMG (E) and HDI were used in amounts shown in Table 2 so that the NCO group/OH group molar ratio of a PTMG (E)/HDI mixture became 15. The properties of urethane prepolymer PE are shown in Table 2. Contrary to urethane prepolymer PA, urethane prepolymer PE was wax like and had no fluidity.

Using urethane prepolymer PE, a coating composition was prepared in substantially the same manner as in Example 1, except that the amounts of the components for the composition were changed as shown in Table 3.

A coating was formed and the properties of the formed coating were evaluated in the same manner as in Example 1. The properties of the coating are shown in Table 3. The drying characteristic of the obtained coating was  
5 far inferior to that of the coating obtained in Example 1 which was prepared using a PTMG having an Mn close to that of PTMG (E).

Further, with respect to the curing agent for the coating composition, which was prepared by mixing urethane prepolymer PE and urethane prepolymer PPCL, the  
10 compatibility of the curing agent with a fluorine type polyol was evaluated by visual observation in the same manner as in Example 1. As a result, it was observed that the film prepared for evaluating the compatibility  
15 of the curing agent was extremely turbid as compared to the film produced in Example 1 in which a PTMG having an Mn close to that of PTMG (E) was used. It has become apparent from this result that the curing agent prepared using urethane prepolymer PE has an unsatisfactory level with respect to the compatibility thereof  
20 with a fluorine type polyol.

#### Comparative Example 2

Urethane prepolymer PF was produced in substantially the same manner as in Example 1, except that  
25

PTMG (F) (commercially available PTMG) having an Mn close to that of PTMG (B) was used instead of PTMG (A), and PTMG (F) and HDI were used in amounts shown in Table 2 so that the NCO group/OH group molar ratio of a PTMG (F)/HDI mixture became 15. The fluidity of urethane prepolymer PF was slightly inferior to that of urethane prepolymer PB. The properties of urethane prepolymer PF are shown in Table 2.

Using urethane prepolymer PF, a coating composition was prepared in substantially the same manner as in Example 1, except that the amounts of components for the composition were changed as shown in Table 3. A coating was formed and the properties of the formed coating were evaluated in the same manner as in Example 1. The properties of the coating are shown in Table 3. The drying characteristic of the obtained coating was far inferior to that of the coating obtained in Example 2 in which a PTMG having an Mn close to that of PTMG (F) was used.

Further, with respect to the curing agent for the coating composition, which was prepared by mixing urethane prepolymer PF and urethane prepolymer PPCL, the compatibility of the curing agent with a fluorine type polyol was evaluated by visual observation in the same manner as in Example 1. As a result, it was observed

that the film prepared for evaluating the compatibility of the curing agent was turbid, differing from the film produced in Example 2 in which a PTMG having an Mn close to that of PTMG (E) was used. It has become apparent from this result that the curing agent prepared using urethane prepolymer PF has an unsatisfactory level with respect to the compatibility thereof with a fluorine type polyol.

Table 2

Raw materials used for producing prepolymers and amounts thereof, and properties of prepolymers

Prepolymer		PA	PB	PE	PF	PPCL
Raw materials	PTMG	A	B	E	F	PCL*
	Amount of PTMG (g)	450	350	450	350	213
	Amount of HDI (g)	616	1013	597	953	945
Yield (g)		525	480	524	472	330
Properties of the pre-polymer	NCO group content (wt%)	3.8	6.9	3.7	6.6	9.4
	HDI concentration (wt%)	0.1	0.1	0.1	0.1	0.1
	Fluidity	○	○	×	△	×

\*: PCL is a polymeric polyol other than PTMG.

Table 3

## Compositions and properties of coating compositions

	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Urethane prepolymer	PA	PB	PE	PF
NCO content (wt%)	3.8	6.9	3.7	6.6
Parts by weight	7.08	5.75	7.15	5.85
Other prepolymer	PPCL	PPCL	PPCL	PPCL
NCO content (wt%)	9.4	9.4	9.4	9.4
Parts by weight	7.08	5.75	7.15	5.85
ACLYDIC A801				
Parts by weight	25.0	25.0	25.0	24.0
Drying characteristic	○	○	△	×
Elongation at break (%)	145	110	123	100
Tensile strength at break (kgf/cm <sup>2</sup> )	122	150	110	132
Compatibility with fluorine type polyol	○	○	×	△

Example 3

A 2-liter flask provided with a thermometer, a refrigerator and a stirrer was charged with 110 g of 4,4'-diphenylmethane diisocyanate (MDI) and 200 g of PTMG (B) produced in Reference Example 2. A reaction was performed at 60 °C for 5 hours with stirring to thereby obtain a urethane prepolymer. 19 g of 1,4-butanediol (hereinafter, referred to simply as "1,4-BD") was added to the obtained urethane prepolymer, and after stirring the resultant mixture for several minutes, the mixture was introduced into a glass mold to thereby obtain a polyether polyurethane in the form of a sheet as a test specimen (dumbbell No. 3). The obtained test specimen was kept in an incubator maintained at 20 °C for 1 week. Subsequently, the hardness, tensile strength at break, and elongation at break (JIS K6301) of the test specimen were evaluated. The results are shown in Table 4.

Comparative Example 3

A polyether polyurethane sheet was produced in substantially the same manner as in Example 3, except that PTMG (F) (commercially available PTMG) was used instead of PTMG (B) in the same molar amount as that of PTMG (B) used in Example 3. The properties of the pro-

duced polyether polyurethane sheet were evaluated. The results are shown in Table 4.

5

Table 4

Properties of polyether polyurethane sheets

	Example 3	Comparative Example 3
PTMG	B	F
Hardness	88	88
Elongation at break (kgf/cm <sup>2</sup> )	465	460
Tensile strength at break (%)	590	540



Example 4

A predetermined amount of PTMG (A) was weighed into a separable flask and dried under a reduced pressure in a nitrogen atmosphere for approximately 2 hours at 80 °C . MDI was added to the dried PTMG (A) so that the NCO group/OH group molar ratio of the resultant mixture became 3.30. In a nitrogen atmosphere, the resultant mixture was placed in an oil bath maintained at approximately 70 °C to thereby synthesize a urethane prepolymer.

1 kg of the synthesized urethane prepolymer was added to a 2-liter vessel and degassed for approximately 40 minutes. Subsequently, 1,4-BD was added to the vessel in an amount wherein the molar ratio of the NCO group of the urethane prepolymer to the OH group of 1,4-BD became 1.03, followed by stirring for approximately 90 seconds to thereby obtain a mixture. The obtained mixture of urethane prepolymer and 1,4-BD was introduced into a mold which had been heated to and maintained at 130 °C, and subjected to crosslinking reaction at 130 °C for 2 hours, thereby obtaining a sheet. The obtained sheet was removed from the mold and subjected to post-crosslinking reaction at 100 °C for 24 hours, thereby obtaining a polyether polyurethane sheet. The tensile strength at break and elongation at break

of the obtained polyether polyurethane sheet were measured in accordance with JIS K6254 (wherein a strip having a width of 5 mm and a thickness of 2 mm was used as a test specimen, the distance between chucks was 30 mm, and the rate of elongation was 10 mm/min (33.33 %/min)). The tensile strength at break and the elongation at break of the strip were 34.3 MPa and 990 %, respectively. Further, a test specimen of the polyether polyurethane sheet was kept at 110 °C to evaluate the degree of discoloration thereof. As a result, it was found that the polyether polyurethane sheet suffered only a slight discoloration.

#### Example 5

After degassing PTMG (A), 92 g (0.05 mol) of PTMG (A) was weighed into a separable flask, and 41.30 g (0.165 mol) of molten MDI was added thereto, thereby obtaining a mixture. (PTMG (A) and MDI were used in amounts wherein the NCO group/OH group molar ratio became 3.30.) The obtained mixture was heated in an oil bath maintained at 80 °C and a reaction was performed while introducing nitrogen gas into the flask and while stirring the mixture in the flask. The NCO group content of the reaction mixture was measured by amine equivalent method, and the reaction was terminated when

the conversion of the OH group in the reaction mixture reached 100 %, thereby obtaining a urethane prepolymer. 100 g of the obtained urethane prepolymer was placed in a stainless steel vessel and 7.54 g (0.0838 mol) of

5 1,4-BD was added thereto (molar ratio of the NCO group of the prepolymer to the OH group of 1,4-BD was 1.03). Immediately after the addition of 1,4-BD, the contents of the stainless steel vessel were stirred for 90 seconds while preventing the formation of the bubbles.

10 The resultant mixture was introduced into a mold and heated at 130 °C for 90 minutes for performing a further reaction, thereby obtaining a polyether polyurethane sheet. The produced polyether polyurethane sheet was removed from the mold and heated at 110 °C

15 for 16 hours to thereby obtain a polyether polyurethane sheet for evaluations of various properties.

The tensile strength at break and elongation at break of the obtained polyether polyurethane sheet were measured (in accordance with JIS K6301 using a dumbbell

20 No. 3 prescribed therein). In addition, the Dunlop impact resilience of the polyether polyurethane sheet was measured. As shown in Table 5, the obtained polyether polyurethane sheet was excellent with respect to the tensile strength at break, the elongation at break and

25 the Dunlop impact resilience.

Comparative Example 4

A polyether polyurethane sheet was produced in substantially the same manner as in Example 5, except  
5 that PTMG (K) (commercially available PTMG) was used instead of PTMG (A) in the same molar amount as that of PTMG (A) used in Example 5.

The tensile strength at break, elongation at break and Dunlop impact resilience of the produced polyether  
10 polyurethane sheet were measured. The results are shown in Table 5.

Comparative Example 5

A polyether polyurethane sheet was produced in  
15 substantially the same manner as in Example 5, except that PTMG (L) (commercially available PTMG) was used instead of PTMG (A) in the same molar amount as that of PTMG (A) used in Example 5.

The tensile strength at break, elongation at break,  
20 and Dunlop impact resilience of the produced polyether polyurethane sheet were measured. The results are shown in Table 5.

Comparative Example 6

25 A polyether polyurethane sheet was produced in

substantially the same manner as in Example 5, except that PTMG (M) (commercially available PTMG) was used instead of PTMG (A) in the same molar amount as that of PTMG (A) used in Example 5.

5           The tensile strength at break, elongation at break and Dunlop impact resilience of the produced polyether polyurethane sheet were measured. The results are shown in Table 5.

10       Comparative Example 7

          A polyether polyurethane sheet was produced in substantially the same manner as in Example 5, except that PTMG (E) (commercially available PTMG) was used instead of PTMG (A) in the same molar amount as that of  
15       PTMG (A) used in Example 5.

          The tensile strength at break, elongation at break and Dunlop impact resilience of the produced polyether polyurethane sheet were measured. The results are shown in Table 5.

Table 5

Properties of polyether polyurethane sheets

	Ex. 5	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
PTMG	A	K	L	M	E
Tensile strength at break (kgf/cm <sup>2</sup> )	510	481	223	380	447
Elongation at break (%)	610	600	530	590	580
Dunlop impact resilience	67.5	66.4	64.6	66	66.4

Example 6

A predetermined amount of PTMG (A) was weighed into a separable flask and dried under reduced pressure in a nitrogen atmosphere for approximately 2 hours at 80 °C. Then, MDI was added to the dried PTMG (A) so that the molar ratio of the NCO group of MDI to the OH group of PTMG became 3.30. In a nitrogen atmosphere, the resultant mixture was placed in an oil bath maintained at approximately 70 °C to thereby synthesize a urethane prepolymer. The NCO group content of the reaction mixture was measured by the amine equivalent method, and the reaction was terminated after confirming that substantially all of the OH groups of PTMG had been reacted.

1 kg of the synthesized urethane prepolymer was added to a 2-liter vessel and degassed for approximately 40 minutes. Subsequently, 1,4-BD was added to the vessel in an amount wherein the molar ratio of the NCO group of the urethane prepolymer to the OH group of 1,4-BD became 1.03, followed by stirring for approximately 90 seconds to thereby obtain a mixture. The obtained mixture of urethane prepolymer and 1,4-BD was introduced into a mold which had been heated to and maintained at 130 °C, and subjected to crosslinking reaction at 130 °C for 2 hours, thereby obtaining a sheet.

The obtained sheet was removed from the mold and subjected to post-crosslinking reaction at 100 °C for 24 hours, thereby obtaining a polyether polyurethane sheet. The raw materials used for producing the polyether polyurethane sheet and the amounts thereof are shown in Table 6.

The stress-strain curve shown in Fig. 3 was prepared using the obtained polyether polyurethane sheet. Further, the tensile strength at break and the elongation at break were measured, and the viscoelasticity index ( $2C_1$ ) was determined from the measured values. The tensile strength at break and the elongation at break were evaluated in accordance with JIS K6254 (wherein a strip having a width of 5 mm and a thickness of 2 mm was used as a test specimen, the distance between chucks was 30 mm and the rate of elongation was 10 mm/min (33.33 %/min)). The results are shown in Table 6.

Further, using the obtained polyether polyurethane sheet, the temperature dependencies of the dissipation factor ( $\tan \delta$ ) and of the storage elastic modulus ( $E'$ ) were evaluated. The results are shown in Figs. 4 and 5, respectively.

A test specimen (having a length of 0.5 cm, a width of 0.5 cm and a thickness of 10 to 100  $\mu$ m) for



microscopic observation was prepared from a part of the obtained polyether polyurethane sheet. A polarization photomicrograph (magnification :  $\times 4,000$ ) of the test specimen was taken under the polarization microscope using crossed Nicols. Another polarization photomicrograph was taken using a sensible color plate. The obtained polarization photomicrographs are, respectively, shown in Figs. 6(a) and 6(b).

#### 10 Comparative Example 8

A polyether polyurethane sheet was produced in substantially the same manner as in Example 6, except that PTMG (L) (commercially available PTMG) was used instead of PTMG (A). The raw materials used for producing the polyether polyurethane sheet and the amounts thereof are shown in Table 6.

The stress-strain curve shown in Fig. 3 was prepared using the polyether polyurethane sheet. Further, the tensile strength at break and the elongation at break were measured, and the viscoelasticity index ( $2C_1$ ) was determined from the measured values. The results are shown in Table 6.

Further, using the polyether polyurethane sheet, the temperature dependencies of the dissipation factor ( $\tan \delta$ ) and of the storage elastic modulus ( $E'$ ) were

evaluated. The results are shown in Figs. 4 and 5, respectively.

The polarization photomicrographs of the polyether polyurethane sheet were taken and shown in Figs. 6(c) and 6(d).

#### Comparative Example 9

A polyether polyurethane sheet was produced in substantially the same manner as in Example 6, except that PTMG (K) (commercially available PTMG) was used instead of PTMG (A). The raw materials used for producing the polyether polyurethane sheet and the amounts thereof are shown in Table 6.

The stress-strain curve shown in Fig. 3 was prepared using the polyether polyurethane sheet. Further, the tensile strength at break and the elongation at break were measured, and the viscoelasticity index ( $2C_1$ ) was determined from the measured values. The results are shown in Table 6.

Further, using the polyether polyurethane sheet, the temperature dependencies of the dissipation factor ( $\tan \delta$ ) and of the storage elastic modulus ( $E'$ ) were evaluated. The results are shown in Figs. 4 and 5, respectively.

The polarization photomicrographs of the polyether

polyurethane sheet were taken and shown in Figs. 6(e) and 6(f).

#### Comparative Example 10

5           A polyether polyurethane sheet was produced in substantially the same manner as in Example 6, except that PTMG (M) (commercially available PTMG) was used instead of PTMG (A). The raw materials used for producing the polyether polyurethane sheet and the amounts  
10           thereof are shown in Table 6.

          The stress-strain curve shown in Fig. 3 was prepared using the polyether polyurethane sheet. Further, the tensile strength at break and the elongation at break were measured, and the viscoelasticity index  
15           ( $2C_1$ ) was determined from the measured values. The results are shown in Table 6.

          Further, using the polyether polyurethane sheet, the temperature dependencies of the dissipation factor ( $\tan \delta$ ) and of the storage elastic modulus ( $E'$ ) were  
20           evaluated. The results are shown in Figs. 4 and 5, respectively.

          The polarization photomicrographs of the polyether polyurethane sheet were taken and shown in Figs. 6(g) and 6(h).

Comparative Example 11

A polyether polyurethane sheet was produced in substantially the same manner as in Example 6, except that PTMG (E) (commercially available PTMG) was used instead of PTMG (A). The raw materials used for producing the polyether polyurethane sheet and the amounts thereof are shown in Table 6.

The stress-strain curve shown in Fig. 3 was prepared using the polyether polyurethane sheet. Further, the tensile strength at break and the elongation at break were measured, and the viscoelasticity index ( $2C_1$ ) was determined from the measured values. The results are shown in Table 6.

Further, using the polyether polyurethane sheet, the temperature dependencies of the dissipation factor ( $\tan \delta$ ) and of the storage elastic modulus ( $E'$ ) were evaluated and shown in Figs. 4 and 5, respectively.

The polarization photomicrographs of the polyether polyurethane sheet were taken and shown in Figs. 6(i) and 6(j).

Table 6

Raw materials used for preparing polyether  
polyurethane sheets and amounts thereof, and  
properties of polyether polyurethane sheets

5

	Ex. 6	Comp. Ex. 8	Com. Ex. 9	Comp. Ex. 10	Comp. Ex. 11
PTMG	A	L (purchased product)	K (purchased product)	M (purchased product)	E (purchased product)
Molar ratio of PTMG/ MDI/ 1,4-BD	1/ 3.30/ 2.25	1/ 3.31/ 2.22	1/ 3.33/ 2.26	1/ 3.30/ 2.24	1/ 3.28/ 2.22
Tensile strength at break $\sigma_b$ (MPa)	34.3	31.9	31.9	32.6	31.9
Elonga- tion at break $\varepsilon_b$ (%)	993	912	896	980	900
$2C_1$	0.92	0.76	0.77	0.83	0.76

As apparent from Fig. 3, the polyether polyurethane of the present invention which was produced (in Example 6) using the specific PTMG (having a narrow molecular weight distribution) exhibited a large elongation at low stress, and the elongation increased in accordance with the increase in the stress applied to the test specimen. Further, as apparent from Table 6, the polyether polyurethane of the present invention had high tensile strength at break and high elongation at break, both of which were higher than exhibited by the polyether polyurethanes of the Comparative Examples. The viscoelasticity ( $2C_1$ ) of the polyether polyurethane of the present invention was also higher than exhibited by the polyether polyurethanes of the Comparative Examples, and these results as well as the photomicrographs of Figs. 6 (a) and 6 (b) show that the phase separation between the hard segment and the soft segment occurred satisfactorily in the polyether polyurethane of the present invention. Specifically, many distinct spherulites are observed in the polarization photomicrographs of the polyether polyurethane of the present invention which are shown in Figs. 6 (a) and 6 (b), which clearly indicates that the phase separation between the hard segment and the soft segment occurred satisfactorily in the polyether polyurethane of the present invention.

The occurrence of such phase separation between the hard segment and the soft segment means that the polyether polyurethane of the present invention has excellent properties required for an elastic material.

5           Further, from the graphs shown in Figs. 4 and 5, it is considered that the polyether polyurethane of the present invention, which is produced using a PTMG having narrow molecular weight distribution, has a uniform relaxation distribution, as compared to those of the  
10 polyether polyurethanes produced in the Comparative Examples using the PTMG's, each having a wide molecular weight distribution. Specifically, in Fig. 4, the polyether polyurethane of the present invention (which is designated as ○ in Fig. 4) exhibits the highest main  
15 dispersion peak (a peak positioned between -100 °C and 50 °C) among the peaks shown in Fig. 4 and, in addition, the width of the peak of the polyether polyurethane of the present invention is the smallest among the peaks shown in Fig. 4. In Fig. 5, with respect to the stor-  
20 age elastic modulus of the polyether polyurethane of the present invention (which is designated as ○ in Fig. 5), the slope (representing the variation of storage elastic modulus in accordance with the change in temperature) in the glass transition region positioned be-  
25 tween -100 °C and 50 °C was much steeper than those of

the polyether polyurethanes obtained in the Comparative Examples. These data also show that the phase separation between the hard segment and the soft segment occurred satisfactorily in the polyether polyurethane of the present invention.

#### Example 7

A polyether polyurethane sheet was produced in substantially the same manner as in Example 6, except that PTMG (B) was used instead of PTMG (A). The raw materials used for producing the polyether polyurethane sheet and the amounts thereof are shown in Table 7.

The polarization photomicrographs of the polyether polyurethane sheet were taken in the same manner as in Example 6. The polarization photomicrographs are shown in Figs. 7(a) and 7(b).

#### Comparative Example 12

A polyether polyurethane sheet was produced in substantially the same manner as in Example 6, except that PTMG (P) (commercially available PTMG) was used instead of PTMG (A). The raw materials used for producing the polyether polyurethane sheet and the amounts thereof are shown in Table 7.

The polarization photomicrographs of the polyether



polyurethane sheet were taken in the same manner as in Example 6. The polarization photomicrographs are shown in Figs. 7(c) and 7(d).

5

Table 7

10 Raw materials used for producing polyether polyurethane sheets and amounts thereof

	Example 7	Comparative Example 12
PTMG	B	P (purchased product)
Molar ratio of PTMG/MDI/1,4-BD	1/3.30/2.24	1/3.26/2.22

15 As clearly shown in Figs. 7(a) to 7(d), many spherulites were observed in the polarization photomicrographs of the polyether polyurethane of the present invention. Thus, it was confirmed that the phase separation between the hard segment and the soft segment occurred satisfactorily in the polyether polyurethane of the present invention.

INDUSTRIAL APPLICABILITY

The polyether polyurethane of the present invention exhibits high elasticity and elastic recovery, low permanent compression set, excellent low-temperature characteristics and high flexibility, as compared to those of the conventional polyether polyurethanes, and can be advantageously used for forming a coating which has no surface tack and is unlikely to suffer discoloration. By virtue of these excellent properties, the polyether polyurethane of the present invention can be used in various application fields related to a flexible foam, a flexible molded foam, a semirigid foam, a rigid foam, a flexible RIM product, a rigid RIM product, a cast polyurethane elastomer, a thermoplastic elastomer, a kneaded elastomer and the like. In addition, the urethane prepolymer of the present invention can be advantageously used for producing the above-mentioned excellent polyether polyurethane. Further, when a composition, such as a coating composition, is prepared using the urethane prepolymer of the present invention, the prepared composition also exhibits excellent properties, such as high fluidity before curing, excellent drying characteristic and capability of forming a coating having no surface tack.

CLAIMS

1. A polyether polyurethane comprising:

(A) at least one polyisocyanate having two or  
5 more isocyanate groups, which is selected from the  
group consisting of an aromatic polyisocyanate and an  
aliphatic polyisocyanate;

(B) a polyoxytetramethylene glycol (PTMG); and

(C) at least one chain extender selected from the  
10 group consisting of a C<sub>2</sub>-C<sub>10</sub> polyol having two or more  
hydroxyl groups and a C<sub>2</sub>-C<sub>10</sub> polyamine having two or  
more amino groups,

wherein said PTMG has the following characteris-  
tics (1) to (3):

15 (1) a number average molecular weight of from 500  
to 4,000;

(2) a molecular weight distribution of 1.75 or  
less in terms of the Mw/Mn ratio, wherein Mw represents  
the weight average molecular weight of PTMG and Mn rep-  
20 represents the number average molecular weight of PTMG;  
and

(3) a content of high molecular weight PTMG mo-  
lecules of 10 % by weight or less, based on the total  
weight of all PTMG molecules, wherein said high molecu-  
25 lar weight PTMG molecules are defined as PTMG molecules

having molecular weights which are at least six times as large as the number average molecular weight of all PTMG molecules.

5        2.    The polyether polyurethane according to claim 1, wherein said PTMG has a heteropolyacid content of from 10 to 900 ppb by weight.

10       3.    The polyether polyurethane according to claim 1, wherein the content of high molecular weight PTMG molecules in said PTMG is 2 to 5 % by weight.

4.    A urethane prepolymer comprising:

15        (A) at least one polyisocyanate having two or more isocyanate groups, which is selected from the group consisting of an aromatic polyisocyanate and an aliphatic polyisocyanate; and

20        (B) a polyoxytetramethylene glycol (PTMG), said urethane prepolymer having terminal isocyanate groups,

wherein said PTMG has the following characteristics (1) to (3):

(1) a number average molecular weight of from 500 to 4,000;

25        (2) a molecular weight distribution of 1.75 or

less in terms of the Mw/Mn ratio, wherein Mw represents the weight average molecular weight of PTMG and Mn represents the number average molecular weight of PTMG; and

5           (3) a content of high molecular weight PTMG molecules of 10 % by weight or less, based on the total weight of all PTMG molecules, wherein said high molecular weight PTMG molecules are defined as PTMG molecules having molecular weights which are at least six times  
10 as large as the number average molecular weight of all PTMG molecules.

5.   The urethane prepolymer according to claim 4, wherein said PTMG has a heteropolyacid content of from  
15 10 to 900 ppb by weight.

6.   The urethane prepolymer according to claim 4, wherein the content of high molecular weight PTMG molecules in said PTMG is 2 to 5 % by weight.

20 7.   The urethane prepolymer according to claim 4, wherein said terminal isocyanate groups are partly or wholly modified to have at least one functional group other than an isocyanate group, wherein said at least  
25 one functional group is introduced to said terminal

isocyanate groups by addition.

8. The urethane prepolymer according to claim 7,  
 wherein said functional group is selected from the  
 group consisting of a (meth)acryloyl group and a silyl  
 group.

ABSTRACT

Disclosed is a polyether polyurethane comprising  
(A) at least one polyisocyanate having two or more iso-  
5 cyanate groups, which is selected from the group con-  
sisting of an aromatic polyisocyanate and an aliphatic  
polyisocyanate; (B) a polyoxytetramethylene glycol  
(PTMG) having a number average molecular weight of from  
500 to 4,000, a molecular weight distribution (Mw/Mn)  
10 of 1.75 or less, and a content of high molecular weight  
PTMG molecules of 10 % by weight or less; and (C) at  
least one chain extender selected from the group con-  
sisting of a C<sub>2</sub>-C<sub>10</sub> polyol having two or more hydroxyl  
groups and a C<sub>2</sub>-C<sub>10</sub> polyamine having two or more amino  
15 groups. Also disclosed is a urethane prepolymer which  
comprises the above-mentioned components (A) and (B)  
and which has terminal isocyanate groups.

Fig.1

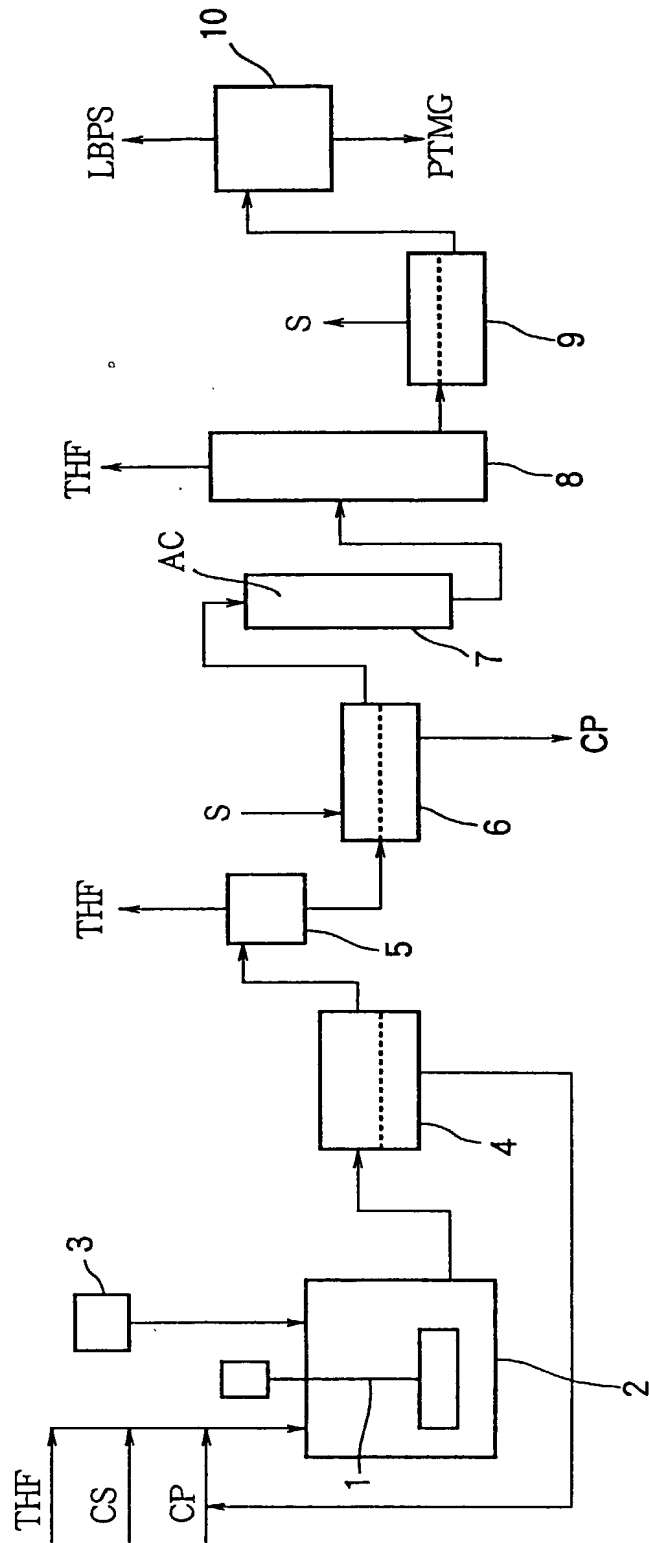




Fig .2

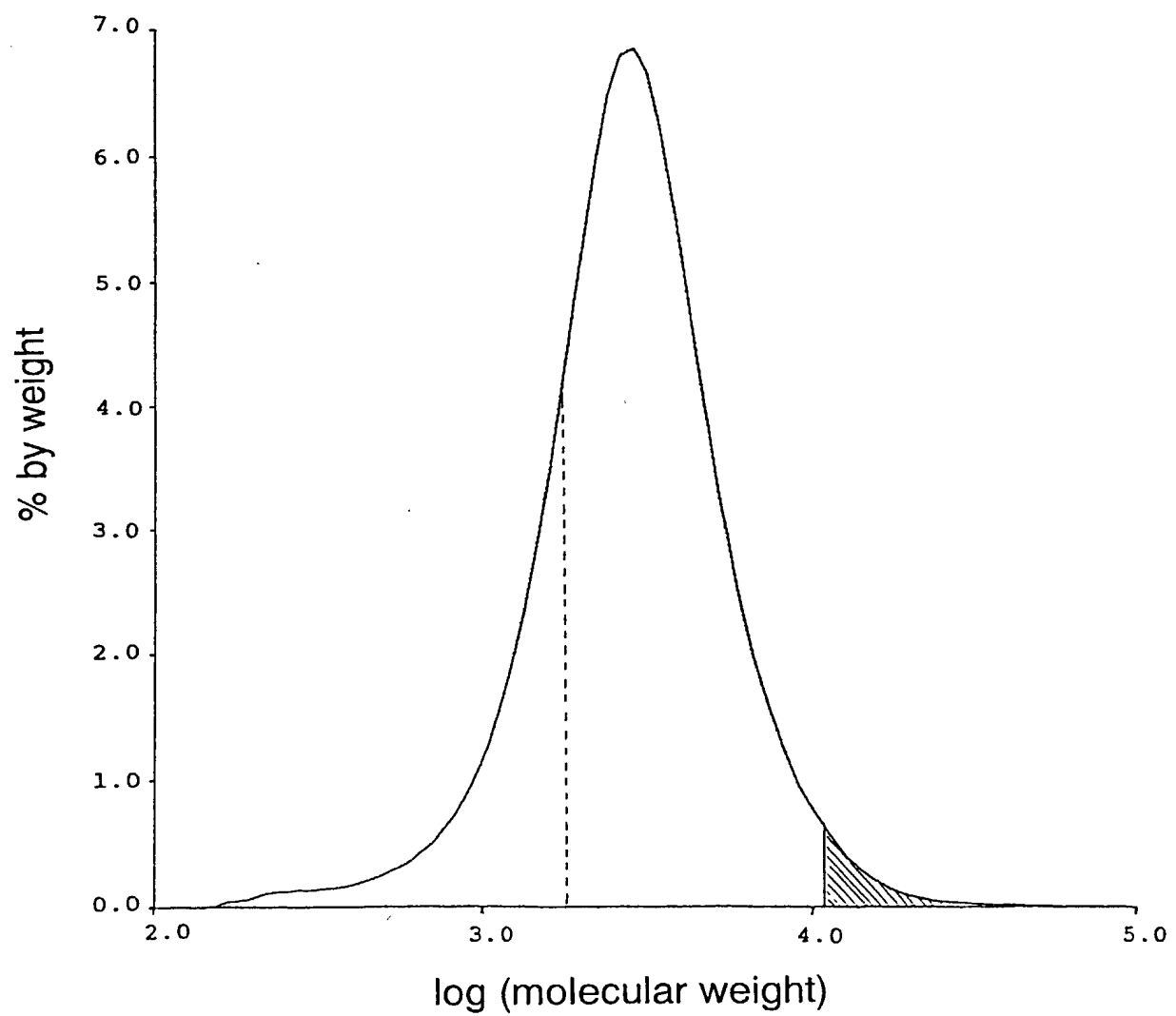


Fig.3

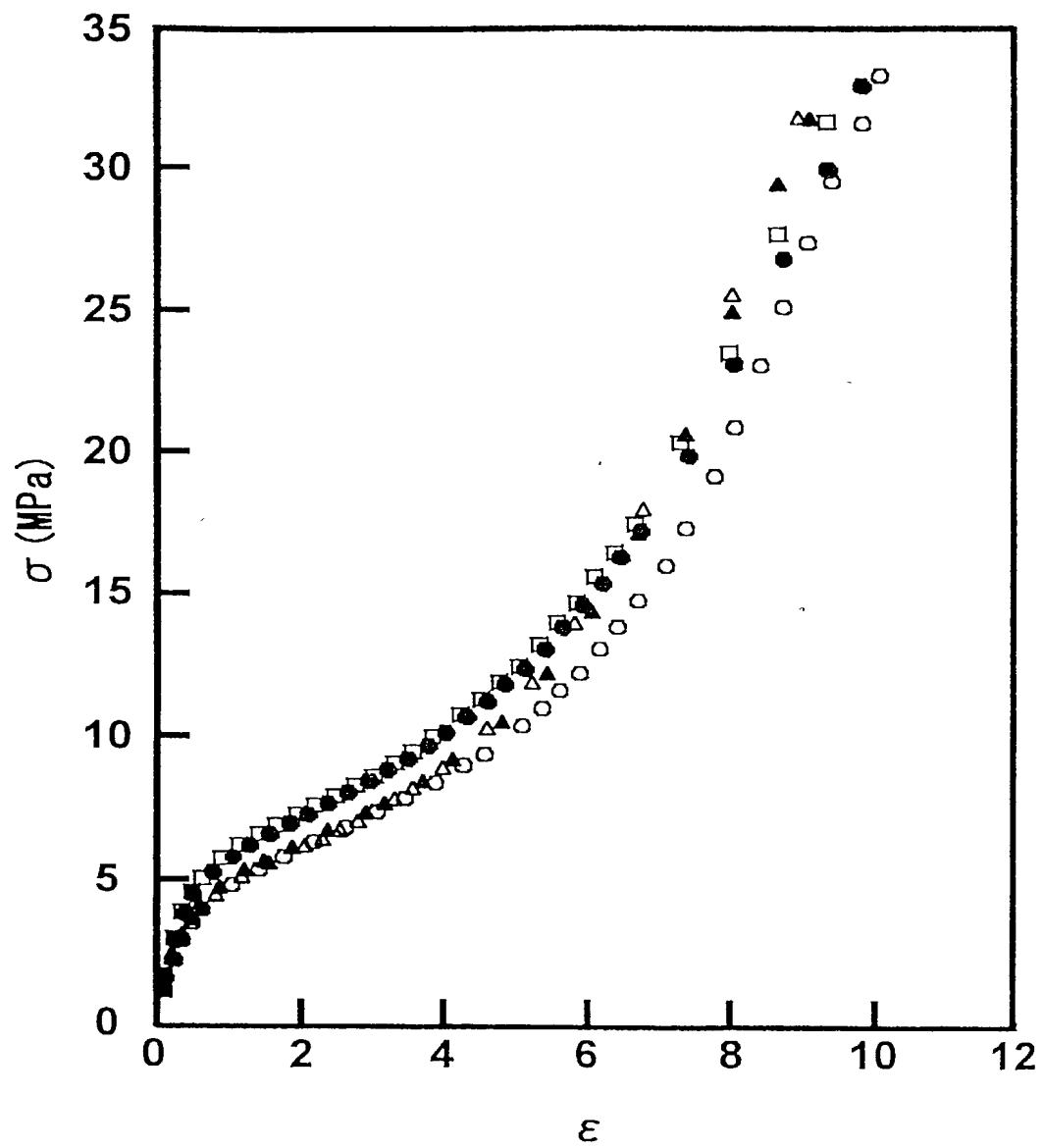


Fig.4

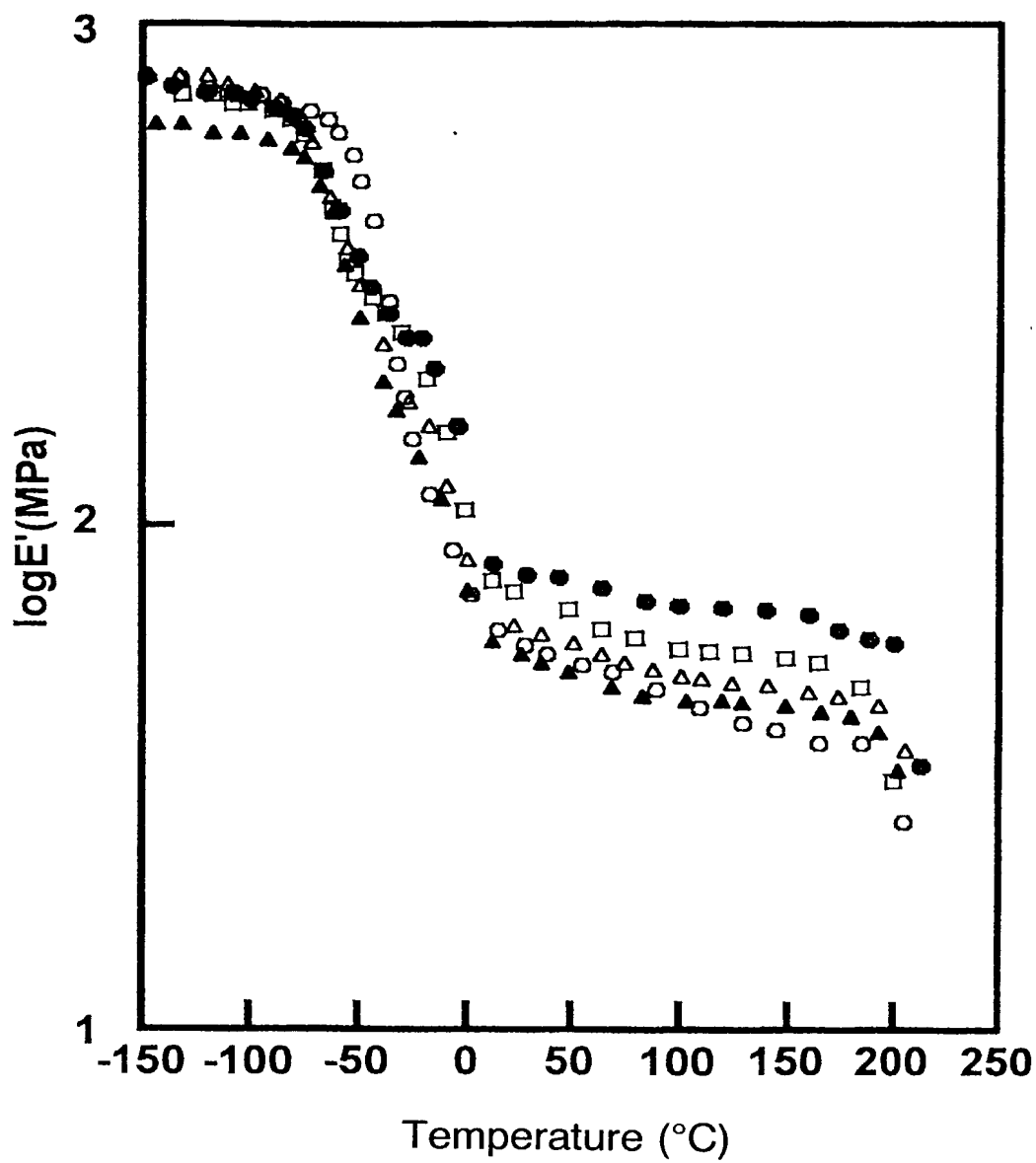


Fig .5

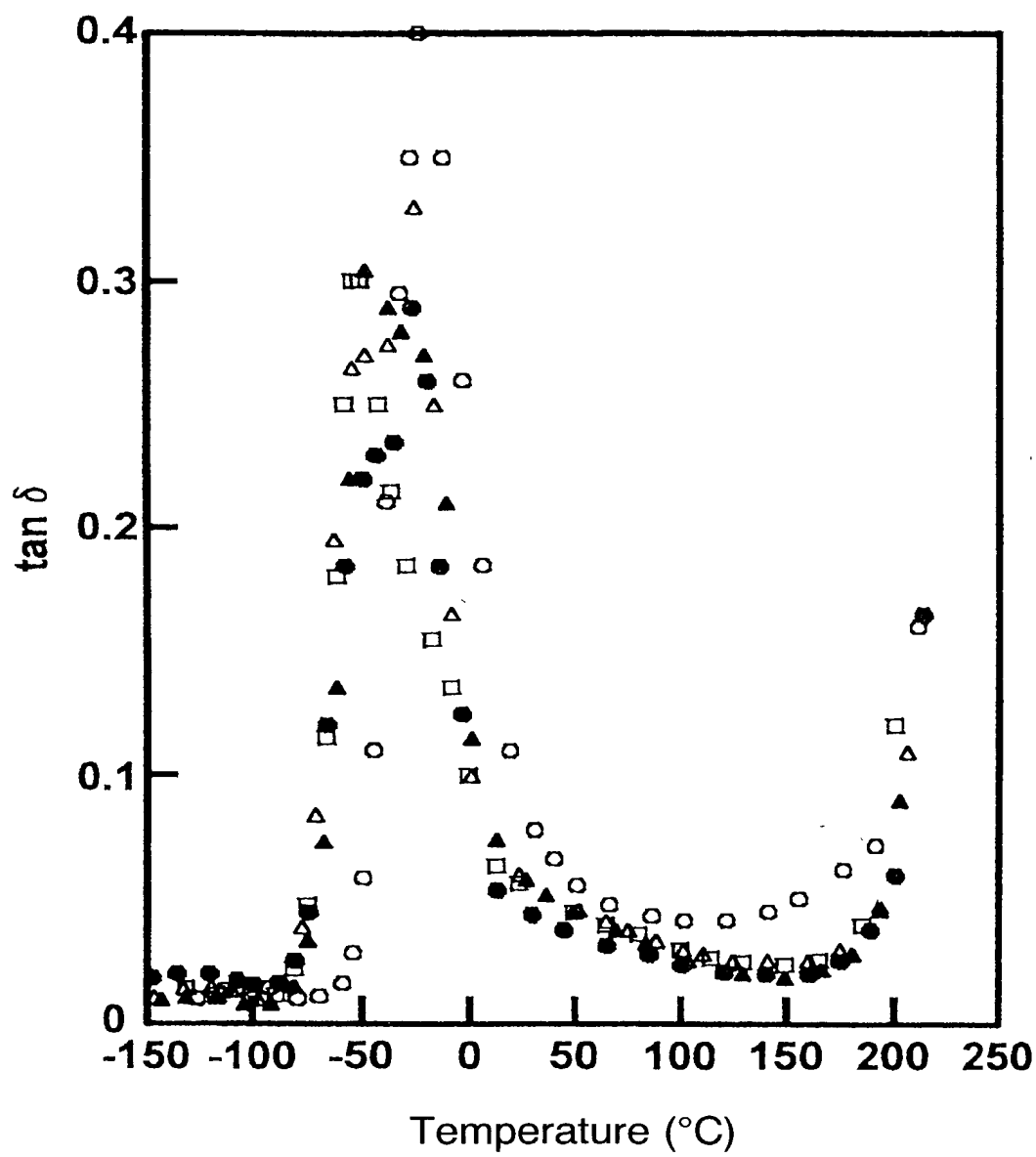


Fig .6(a)

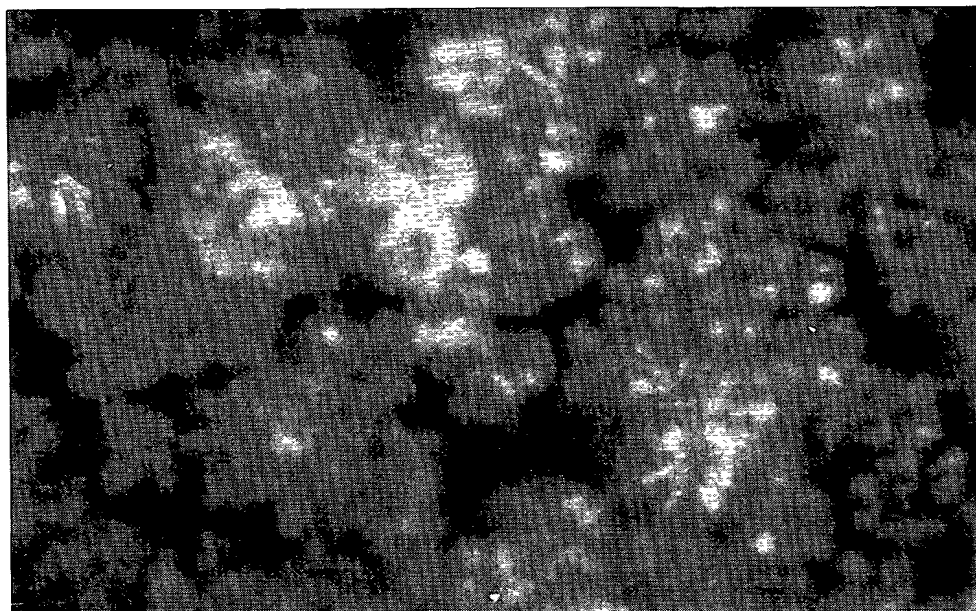


Fig .6(b)

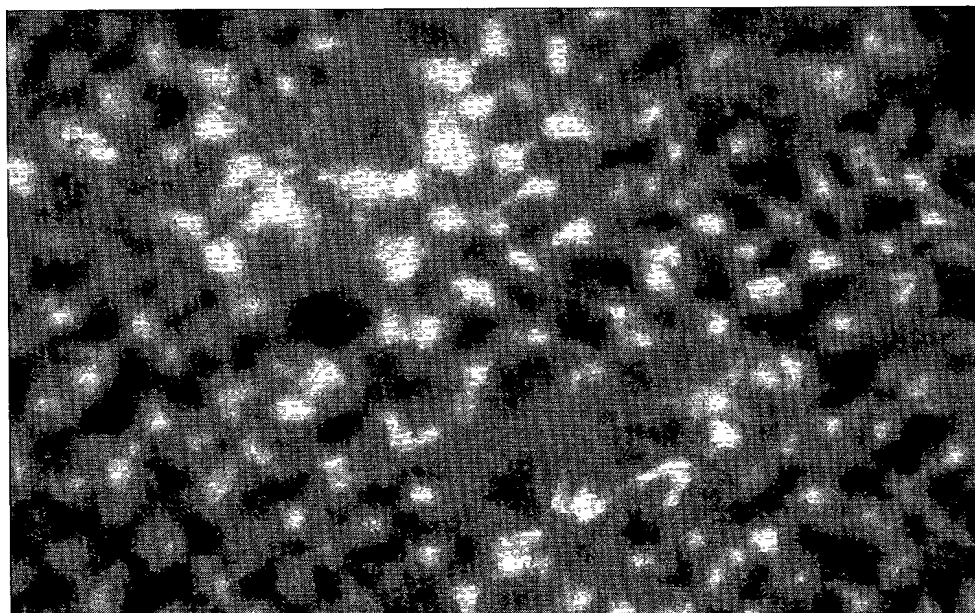


Fig .6(c)

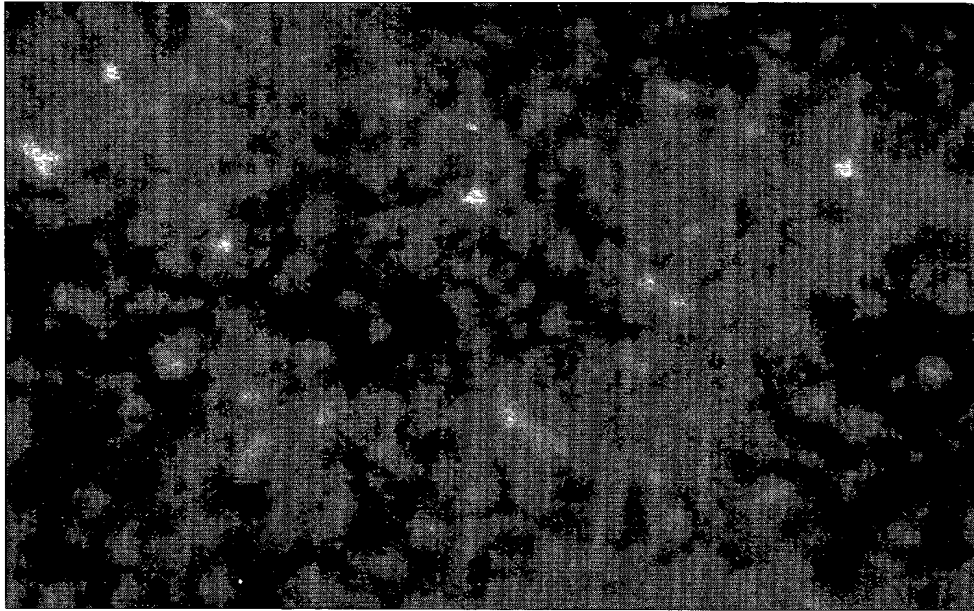


Fig .6(d)

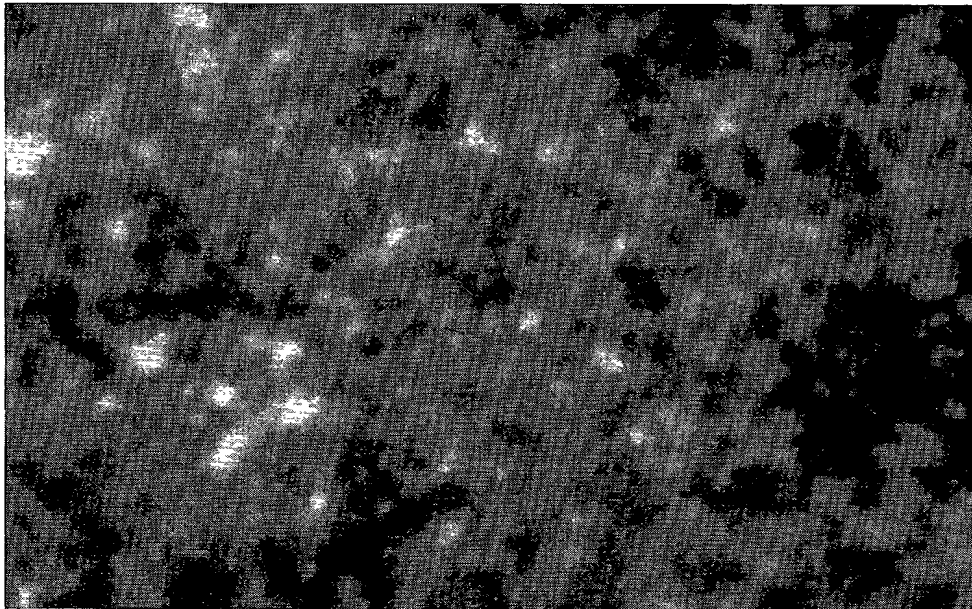


Fig .6(e)

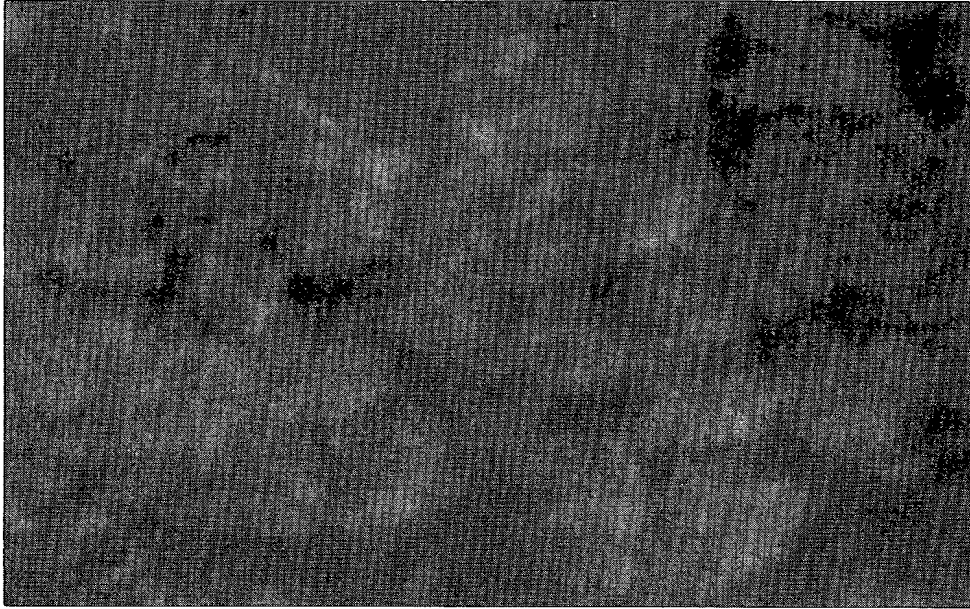


Fig .6(f)

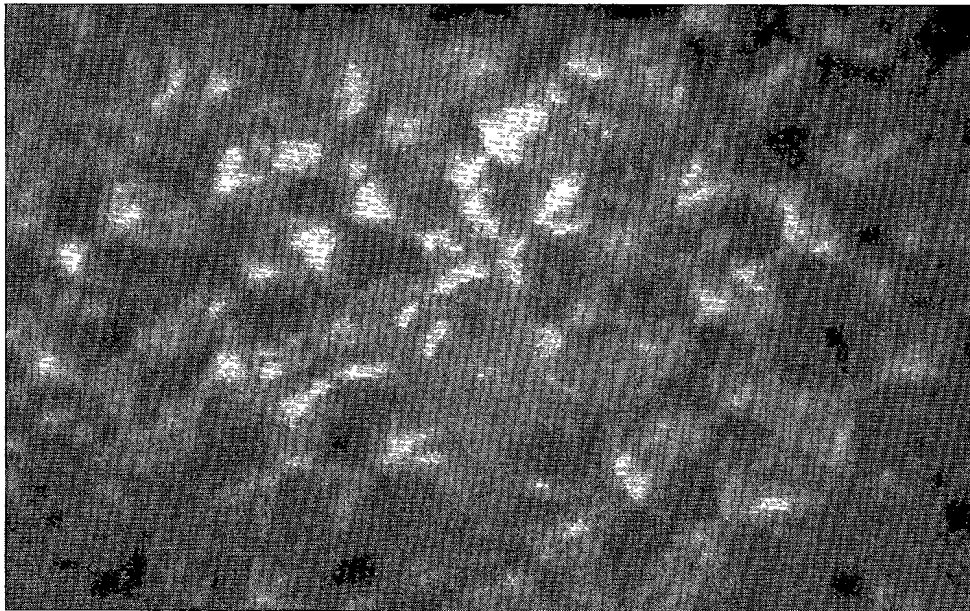


Fig .6(g)

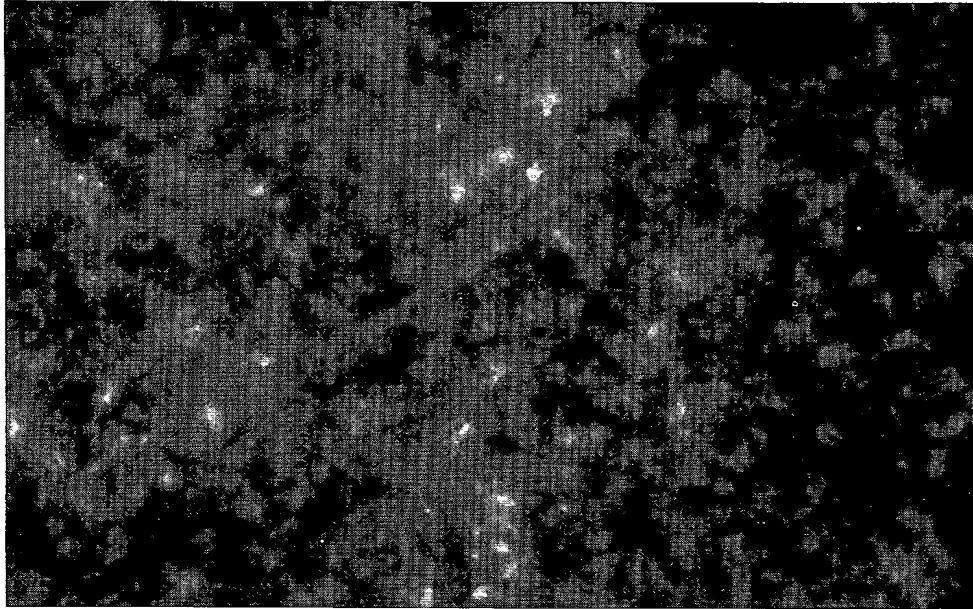


Fig .6(h)

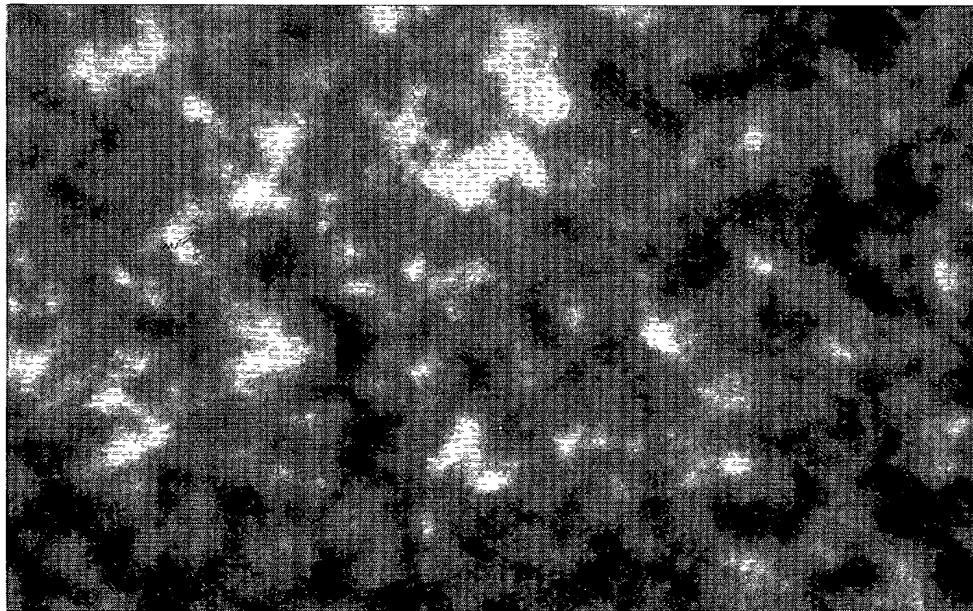




Fig .6(i)

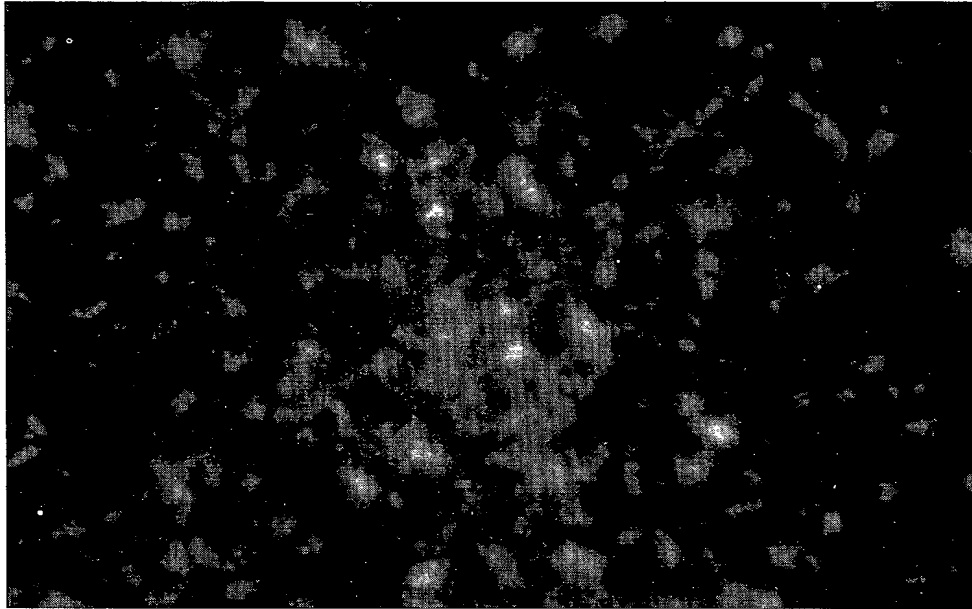


Fig .6(j)

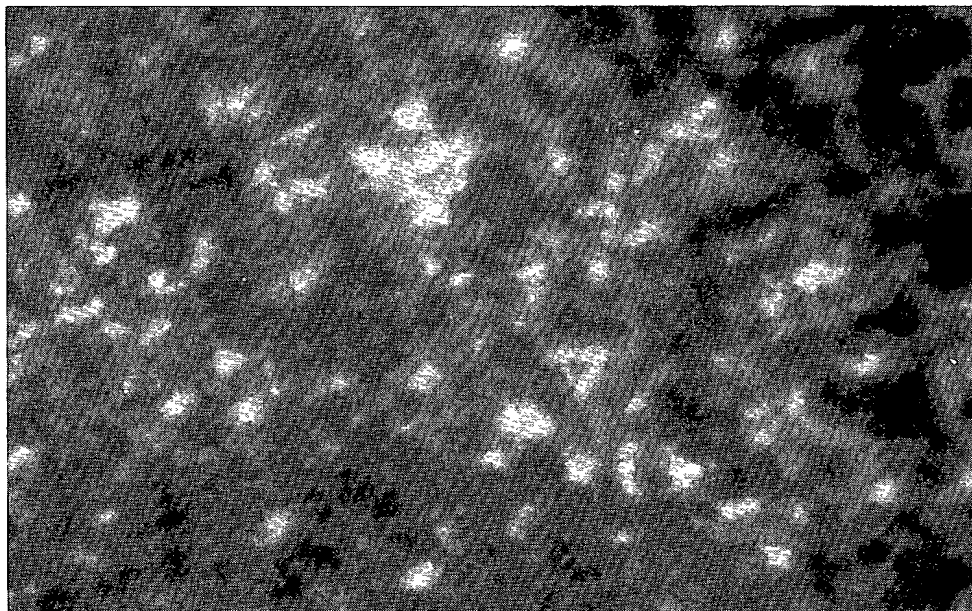


Fig.7(a)

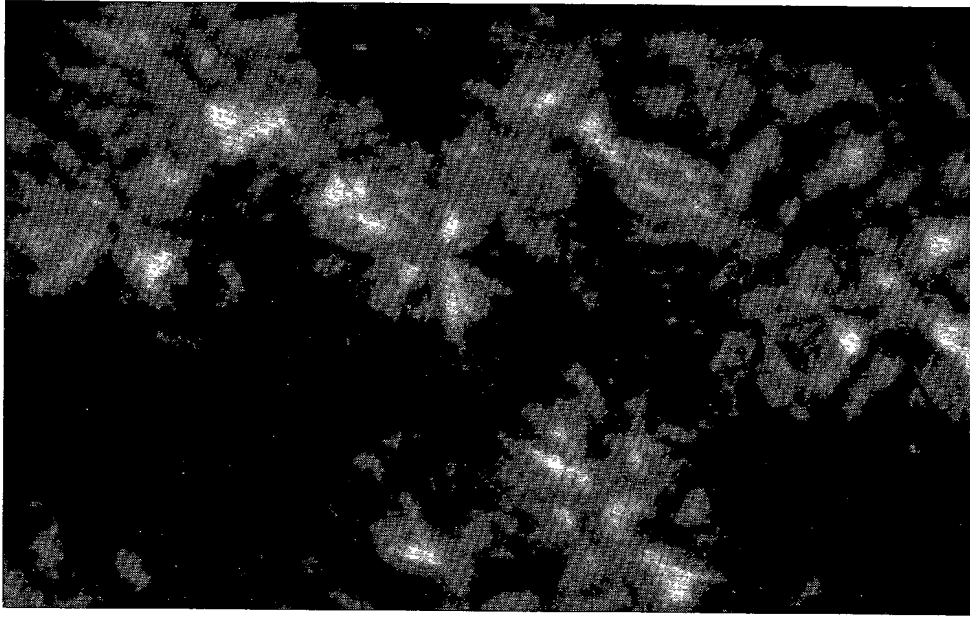


Fig.7(b)

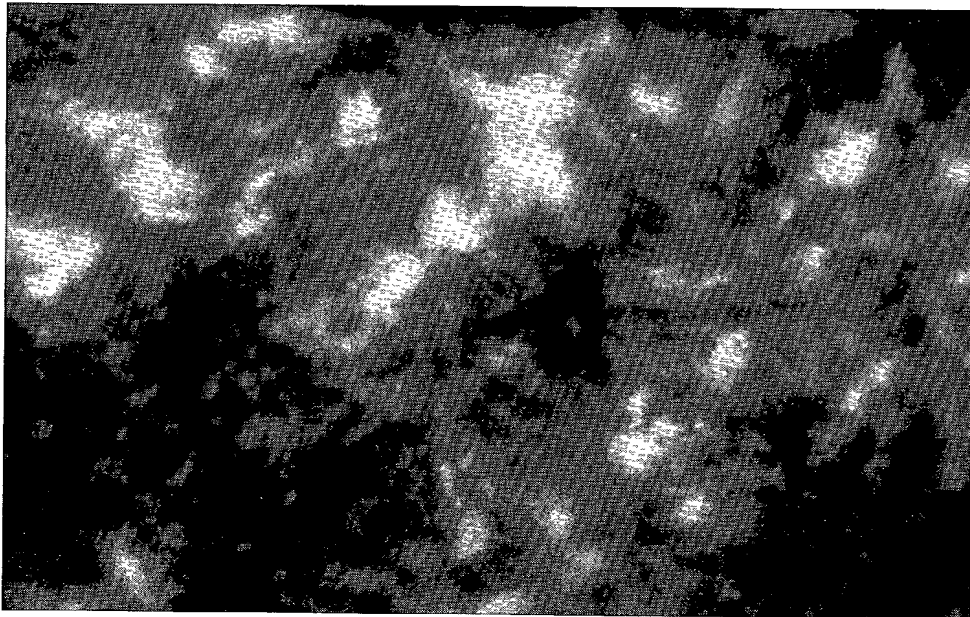


Fig.7(c)

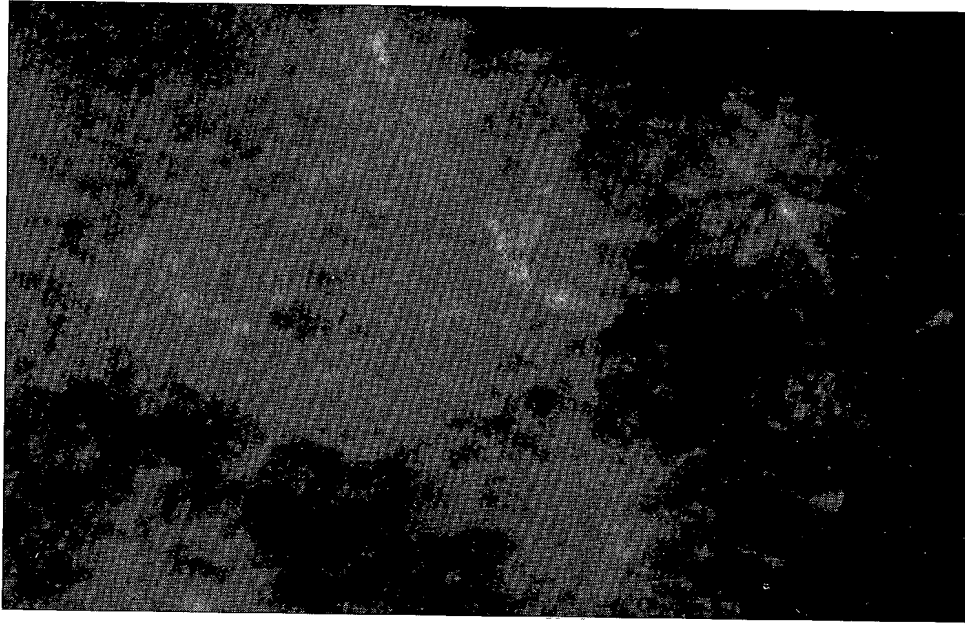
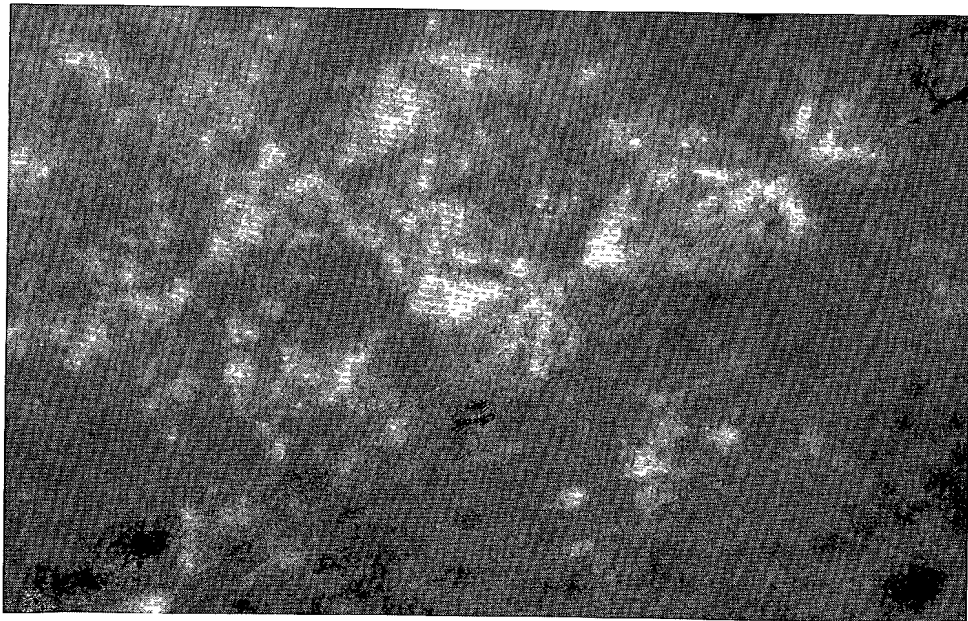


Fig.7(d)



## BIRCH, STEWART, KOLASCH &amp; BIRCH, LLP

## COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO.

0216-0466P

PLEASE NOTE:  
YOU MUST  
COMPLETE THE  
FOLLOWING:

Insert Title:

Polyether polyurethane

Fill in Appropriate  
Information -  
For Use Without  
Specification  
Attached:

the specification of which is attached hereto. If not attached hereto,

the specification was filed on \_\_\_\_\_ as

United States Application Number \_\_\_\_\_; and /or

the specification was filed on August 18, 2000 as PCT

International Application Number PCT/JP00/05570; and was

amended under PCT Article 19 on \_\_\_\_\_ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Insert Priority  
Information:  
(if appropriate)

## Prior Foreign Application(s)

11-233017

Japan

08/19/1999

Priority Claimed

☒ Yes ☐ No

Yes No

☐ Yes ☐ No

Yes No

☐ Yes ☐ No

Yes No

☐ Yes ☐ No

Yes No

☐ Yes ☐ No

Yes No

(Number)

(Country)

(Month/Day/Year Filed)

(Number)

(Country)

(Month/Day/Year Filed)

(Number)

(Country)

(Month/Day/Year Filed)

(Number)

(Country)

(Month/Day/Year Filed)

(Number)

(Country)

(Month/Day/Year Filed)

Insert Provisional  
Application(s):  
(if any)

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More Than 12 Months (6 Months for Designs) Prior To The Filing Date of This Application:

Insert Requested  
Information:  
(if appropriate)

Country

Application No.

Date of Filing (Month/Day/Year)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Insert Prior U.S.  
Application(s):  
(if any)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

10049827 0216-0466P

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

Terrell C. Birch	(Reg. No. <u>19,382</u> )	Raymond C. Stewart	(Reg. No. <u>21,066</u> )
Joseph A. Kolasch	(Reg. No. <u>22,463</u> )	James M. Slattery	(Reg. No. <u>28,380</u> )
Bernard L. Sweeney	(Reg. No. <u>24,448</u> )	Michael K. Mutter	(Reg. No. <u>29,680</u> )
Charles Gorenstein	(Reg. No. <u>29,271</u> )	Gerald M. Murphy, Jr.	(Reg. No. <u>28,977</u> )
Leonard R. Svensson	(Reg. No. <u>30,330</u> )	Terry L. Clark	(Reg. No. <u>32,644</u> )
Andrew D. Meikle	(Reg. No. <u>32,868</u> )	Marc S. Weiner	(Reg. No. <u>32,181</u> )
Joe McKinney Muncy	(Reg. No. <u>32,334</u> )	Donald J. Daley	(Reg. No. <u>34,313</u> )
C. Joseph Faraci	(Reg. No. <u>32,350</u> )		

Send Correspondence to:

**BIRCH, STEWART, KOLASCH & BIRCH, LLP**

**P.O. Box 747 • Falls Church, Virginia 22040-0747**

**Telephone: (703) 205-8000 • Facsimile: (703) 205-8050**

PLEASE NOTE:  
YOU MUST  
COMPLETE THE  
FOLLOWING:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of First or Sole  
Inventor:  
Insert Name of Inventor  
Insert Date This  
Document is Signed

Insert Residence  
Insert Citizenship

Insert Post Office  
Address

Full Name of Second  
Inventor, if any

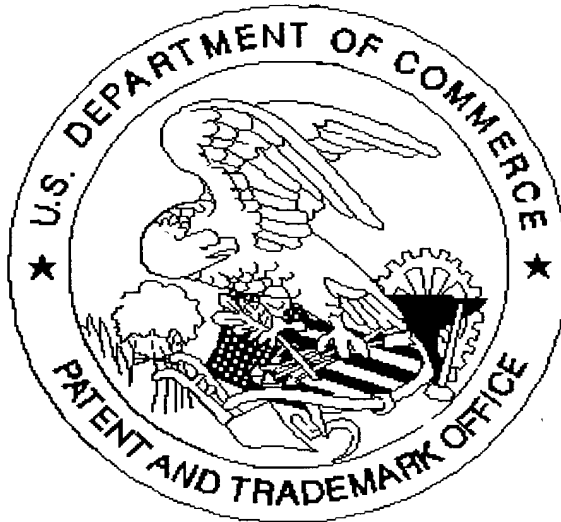
Full Name of Third  
Inventor, if any

Full Name of Fourth  
Inventor, if any

Full Name of Fifth  
Inventor, if any

GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Atsushi	SHIMIZU	Atsushi Shimizu	Feb. 10, 2002
Residence (City, State & Country)		CITIZENSHIP	
Fuchu-shi, Tokyo, Japan JPX		Japanese	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			
3-14-3-210, Musashidai, Fuchu-shi, Tokyo 183-0042 JAPAN			
GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Mutsuhisa	FURUKAWA	Mutsuhisa Furukawa	Feb. 10, 2002
Residence (City, State & Country)		CITIZENSHIP	
Nagasaki-shi, Nagasaki-ken, Japan JPX		Japanese	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			
3-35-19, Yokoo, Nagasaki-shi, Nagasaki-ken 852-8065 JAPAN			
GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Kiyoo	KATO	Kiyoo Kato	Feb. 10, 2002
Residence (City, State & Country)		CITIZENSHIP	
Kawasaki-shi, Kanagawa-ken, Japan JPX		Japanese	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			
537-10, Nogawa, Miyamae-ku, Kawasaki-shi, Kanagawa-ken 216-0001 JAPAN			
GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Yoshiyuki	ASAHINA	Yoshiyuki Asahina	Feb. 10, 2002
Residence (City, State & Country)		CITIZENSHIP	
Nobeoka-shi, Miyazaki-ken, Japan JPX		Japanese	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			
1-18-4, Sakuragaoka, Nobeoka-shi, Miyazaki-ken 882-0007 JAPAN			
GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			

United States Patent & Trademark Office  
Office of Initial Patent Examination -- Scanning Division



Application deficiencies found during scanning:

☐ Page(s) \_\_\_\_\_ of \_\_\_\_\_ were not present  
for scanning. (Document title)

☐ Page(s) \_\_\_\_\_ of \_\_\_\_\_ were not present  
for scanning. (Document title)

☐ *Scanned copy is best available. Drawing are very dark*